

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0705-0188	
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE January 10, 2000	3. REPORT TYPE AND DATES COVERED 61 Aug 98 - 31 Jul 01 Technical Repts. # 4, 5, 6 and 7	
4. TITLE AND SUBTITLE Mechanics of Powder Plastic Powder Compacts			5. FUNDING NUMBERS DAAG55-98-1-0455	
6. AUTHOR(S) PII: Fred F. Lange				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Materials Department College of Engineering University of California Santa Barbara, CA 93106-5050			8. PERFORMING ORGANIZATION REPORT NUMBER NA	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING/MONITORING AGENCY REPORT NUMBER ARO 38100.1-MS	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12A. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12B. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Colloidal Isopressing is a new method for the shaping of ceramic components from powder suspensions in a rapid and cost effective manner. Colloidal Isopressing starts with a slurry containing a relatively low volume fraction of powder, where the particles weakly attracted to one another due to a short-range repulsive potential developed during slurry formulation. The slurry is pre-consolidated to a high relative density at a pressure that will allow the consolidated body to be easily fluidized. The fluidized body is injected into a rubber mold, which is subjected to a high pressure in an isopressure. The high pressure pushes the particles into contact to convert the fluid-like body into an elastic body that can be removed from the rubber mold without distorting its shape. The unique attributes of Colloidal Isopressing is that complex shaped bodies can be rapidly produced that do not shrink during drying. The short-range repulsive potential required to produce a fluid-like, pre-consolidated body is developed during slurry formulation by adding excess salt to a dispersed slurry produced either by the electrostatic double layer approach (adjusting pH), or attaching short molecules to the surface of the particles. It is the short-range repulsive potential that prevents a large fraction of the particle from being pushed into contact during pre-consolidation at low pressures, and therefore allows the pre-consolidated body to be fluidized to fill a rubber mold. In much of our work, the electrostatic double layer approach is used to produce the initial dispersed slurry, and NH_4Cl was added to change the long-range repulsive potential to a short-range repulsive potential.				
14. SUBJECT TERMS			15. NUMBER OF PAGES 51 pages	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

20010302 088

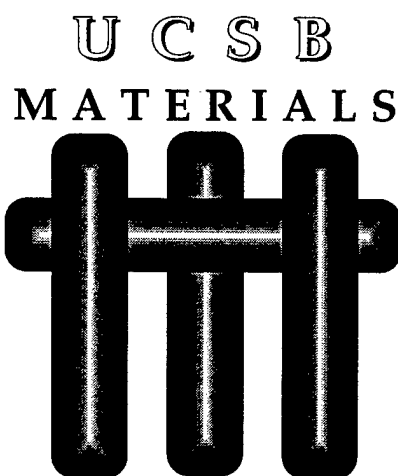
Technical Reports #4, 5, 6, 7

(Period ending 31 December 2000)

Contract Number: DAAG55-98-1-0455

**"The Mechanics of Plastic Powder Compacts: The Development of
Shape Forming Science"**

Principle Investigator: F. F. Lange



**Materials Department
University of California, Santa Barbara
Santa Barbara, CA 93106**

**F. F. Lange
Materials Dept., UCSB**

Technical Report # 4

January 25, 2001

Contract Number: DAAG55-98-1-0455

in press with Advanced Materials

Colloidal Isopressing: A New Shape Forming Method

Benjamin C. Yu and Frederick F. Lange

Materials Department, University of California, Santa Barbara
Santa Barbara, California 93106, USA

Abstract

Colloidal Isopressing is a rapid method to form an engineering shape from a powder slurry, previously filtered to remove strength degrading inclusions. A slurry composed of a weakly attractive particle network, produced with a short-range, repulsive interparticle pair potential, is consolidated to make a body with a high particle density that is easily fluidized by vibration. The fluid-like body is injected into a rubber mold and subjected to a larger isostatic pressure to force particles into contact. This creates a strong, elastic body with the shape of the rubber mold. Because the particles are forced into contact at a high pressure, the liquid remaining within the component can be removed by evaporation without shrinkage, avoiding fracture during rapid drying.

Ceramic components, ranging from silicon nitride turbocharger rotors used in high-performance automobiles to translucent aluminum oxide tubes used in high efficiency yellow sodium lamps, are formed by molding a powder into the desired engineering shape. The powder compact is then densified to its final form by a high temperature heat treatment. Because advanced ceramic powders such as silicon nitride and alumina lack the plastic properties of traditional clay-based ceramics, conventional shape forming is carried out by either the pressure consolidation of a dry powder or by the pressure forming of a powder containing a large fraction of a polymer that imparts plasticity. Both of these commercial shaping methods suffer from inclusions, present in the powder and retained during shape forming and densification. These inclusions concentrate any applied stress to severely degrade the component's strength. In addition, the large quantity of polymer required for plastic forming (on the order of 40% by volume) must be removed very slowly to avoid defect formation.

It is possible to improve the reliability of ceramic components by processing the powder as a colloidal suspension [1]. When the ceramic particles are dispersed in a liquid, the slurry can be passed through a filter to remove all inclusions greater than the size defined by the filter. Reducing the inclusion size will increase the average strength

and component reliability. Techniques currently employed to form engineering shapes from a slurry can be categorized as either consolidation or direct shaping methods.

Consolidation methods start with a slurry containing a low volume fraction of powder that is concentrated by either evaporation or pressure filtration. Examples include tape casting (evaporation) [2], slip casting (capillary pressure via a porous mold) [4], and pressure filtration (external overpressure) [3]. Because the initial volume fraction of powder is < 0.40 , these dispersed slurries can first be passed through a filter to remove strength degrading inclusions. Consolidation methods also have the capability to produce bodies with the highest relative density. However, because the liquid removed during consolidation must flow through the body as it consolidates, these methods generally require long periods within the mold. Additionally, tape casting and slip casting, are typically limited to thin (or thin walled) bodies.

Direct shaping methods start with a slurry containing a high volume fraction of powder (> 0.50) that can still be either poured or injected into a mold. Unlike the consolidation methods, the volume fraction of powder does not change during molding. Highly repulsive interparticle potentials are needed to formulate flowable slurries containing a high volume fraction of powder. Within the mold, the slurry must be converted to an elastic body so the component can retain its shape upon removal from the mold. Direct shaping methods include injection molding [5], Gel Casting [6], Direct Coagulation Casting [7] and VibraForming [8]. In the case of injection molding and gel casting, the slurry's liquid phase solidifies by either freezing or polymerization, respectively. For Direct Coagulation Casting and VibraForming, the particle network within the slurry is solidified by changing the pH of the slurry to the isoelectric point (the pH where the net surface charge on the particle is zero) via a temperature induced chemical reaction. Because slurries used for all direct shaping methods must contain the highest volume fraction of powder possible, they are too viscous to remove strength degrading inclusions by filtration. Although injection molding only requires very short periods within the mold, very long periods are needed to remove the polymer without causing cracking, blistering, etc. The periods required to convert the molded slurry into an elastic body is too long (10 minutes to several hours) to utilize either Gel Casting, Direct Coagulation Casting or VibraForming as rapid forming methods.

After a component is shaped by any one of these methods, the liquid within the powder compact must be removed before densification at high temperature. Shrinkage typically occurs during evaporative drying because the powder can further consolidate, driven by capillary (Laplace) pressure. Surface tensile stresses associated with shrinkage may arise if the exterior portion of the body, where evaporation initiates, is constrained by the interior. The magnitude of the tensile stress, which can induce cracking, depends on a number of factors including the initial relative density achieved during shape forming and the rate of drying [9]. Bodies produced by direct shaping methods are more prone to cracking because they exhibit greater shrinkage relative to the higher density, consolidated bodies.

Pujari *et al.* [10] have shown that the average strength and reliability of tensile specimens can be greatly improved by filtering inclusions from slurries prior compact formation by pressure filtration. Unfortunately, most of the colloidal forming methods described above have only found niche industrial applications. For example, tape casting is one viable technique for fabrication of multilayer electronic packages. In general, the long forming periods, large fractions of polymer that must be removed prior to densification, and/or the inability to remove inclusions prior to shaping are the limiting factors for economical, industrial practice.

Colloidal Isopressing, the method introduced here, has attributes of both the consolidation and direct shaping methods. This method was first demonstrated after the discovery that particles held apart by a short-range repulsive potential can be pushed into contact during consolidation when the applied pressure is greater than a critical value [11]. When the slurry is consolidated below the critical pressure, the consolidated body can be made to flow at a stress that is governed by the interparticle pair potential formulated in the slurry state. At pressures above this critical value, the consolidated body exhibits elastic behavior. We use this plastic-to-elastic transition by first consolidating a body below the critical pressure, injecting the fluid-like body into a rubber mold, then isopressing the filled mold above the critical pressure. The high isostatic pressure acts to convert the fluid-like material to an elastic body that can be removed from the rubber mold without shape distortion. Above the critical consolidation pressure, the particles are forced into contact and pack to their highest relative density. Therefore, the liquid that remains can be rapidly removed by evaporation without either shrinkage or cracking.

The Colloidal Isopressing method requires a slurry formulation wherein the particles are attracted to one another by the pervasive van der Waals potential, but are prevented from touching with a short range repulsive potential. The van der Waals potential always causes particles of the same material to be attractive when the surrounding fluid has a different dielectric constant. By itself, the van der Waals potential produces a network of particles in elastic contact. Due to friction, touching particles are difficult to rearrange during consolidation and therefore do not produce the highest relative density [12]. To keep the particles apart, low density matter that does not significantly contribute to the van der Waals potential must shroud the particles and cause an increase in the free energy when the shrouds of approaching particles interact. The interpenetrating shrouds keep the particles apart and, in effect, shield either a portion or all of the attractive van der Waals potential. When the electrostatic double layer method (approximated by the DLVO theory [13]) is used to produce a repulsive potential, counterions comprise the shroud. When the steric approach is used, the shroud is composed of molecules, e.g. linear molecules bonded to the surface and extending into the surrounding fluid. Here, we demonstrate the Colloidal Isopressing method with the use of counterions and commercial α - Al_2O_3 powders (Sumitomo Chemical Co., Grade AKP-50, 0.24 μm diameter; AKP-30, 0.40 μm ; and AKP-15, 0.65 μm) with an iso-electric point at pH 9.

A well dispersed, 0.20 solid volume fraction slurry was created by sonicating alumina powder in deionized water (initial resistivity $\sim 17.5 \times 10^6 \Omega\text{-cm}$) adjusted to pH 4 with nitric acid. The addition of 0.5M NH_4Cl developed a weakly attractive potential between the particles by reducing the extent of electrostatic double layer repulsion. As previously reported [11], the addition of 0.5M NH_4Cl to a dispersed alumina slurry produces a plastic-to-elastic transition at a consolidation pressure of 65 MPa. After the slurry was consolidated by pressure filtration at 5 MPa, the powder within the saturated compact had a relative density of 0.575 ± 0.010 (see Table I) and could be made to flow with a rheology that resembles toothpaste after moderate vibration (a compressive flow stress of ≈ 0.01 MPa). The fluidized alumina body was extruded into a rubber mold and vibrated to allow any air bubbles, trapped in the mold during filling, to rise to the surface (the viscosity of these weakly attractive particle exhibits shear thinning behavior).

The molds were fabricated by casting silicone rubber (GE Silicones, RTV664) around an appropriate shape. Examples shown in Figure 1 include (a) an engine valve used as a proof of concept, and (b) a rectangular prism (12.7×6.4 mm in cross section), used to determine the properties of the isopressed material. The mold must contain some porosity to absorb a small amount of water during isopressing; otherwise the liquid surrounding the particles would sustain the applied hydrostatic pressure and shield the particle network. This was achieved by placing a small amount of dry powder at one end of the mold cavity. An isostatic pressure in the range of 100 to 300 MPa, much greater than the plastic-to-elastic transition pressure, was applied for a period between 15 seconds to 10 minutes. After iso-pressing, the elastic specimens were ejected from the mold.

Table 1 lists the relative density, determined by the weight loss during drying at 70°C and heating at 500°C to account for the loss of water and NH_4Cl , respectively. The relative density after isopressing was independent of the isopressure for periods ≥ 20 seconds. For shorter periods at the lowest pressure (100MPa), the end furthest from the dry powder was still plastic, indicating that the hold time was insufficient to transport water through the entire 50 mm long bar. The differential equation developed by Darcy to describe the flow of a liquid through a porous body can be used to determine the minimum time needed to produce an elastic body throughout the mold cavity. Application of Darcy's Law reveals that the very short period needed to convert the fluid paste to an elastic compact is primarily due to the very small change in relative density (see Table 1) after the short isopressing period. That is, only a small amount of liquid needs to be removed to convert the fluid paste to an elastic body.

The saturated strength of bars ($12.7 \times 6.4 \times 50$ mm) formed with the Colloidal Isopressing method was measured in 3-point bending. Efforts to minimize loss of water from the consolidated body were made by testing in a humid environment immediately upon removal from the mold. The strength and relative density as a function of applied isopressure for alumina compacts composed of the finest particle size (AKP-50) are shown in Figure 2. Both the strength and relative density were invariant with respect to the applied isostatic pressure in the range between 100 MPa and 300MPa. These observations indicate that a stable particle network is achieved at an isopressure of 100 MPa and that the network does not change with increased pressure. It should be noted that the strengths reported in Figure 2 are nearly identical to those for dry pressed alumina bars containing a polymer binder tested in flexure (3-4.5 MPa) [14]. This is significant because the isopressed bodies studied here did not require any polymer binder to achieve the same high green strengths.

It was observed that the surface of the mold transferred extremely well to the isopressed body as indicated by the engine valve produced with the Colloidal Isopressing method (Figure 1a). The silicone rubber mold (center) was cast around a metallic engine valve, and a porous piece of alumina (not pictured) was used against the base of the valve to accommodate fluid squeezed out during isopressing. The component produced from this mold (far right) has been sintered and is smaller due to shrinkage associated with densification. However, it is clear that the corners and surfaces were all transferred to the isopressed component very well. Similarly, the bar shaped compact in Figure 1b has the same shape as the mold cavity. The corners remain sharp and edges true because the change in volume during shape forming is minimized.

It was determined that the isopressed bodies maintain their shape during drying and sintering. Saturated specimens placed directly into a 70°C drying oven never cracked during drying, and no shrinkage was detected (within 0.3 percent of linear dimension). Rapid drying under controlled heating rates, from room temperature to 300°C, was monitored by thermogravimetric analysis for bar specimens (12.7 x 6.4 x 50 mm). Rates up to 30°C per minute were not found to cause any damage, while a few specimens dried at 40°C per minute shattered. Figure 3 shows a 30°C/min drying run; the maximum rate of weight loss is about 14% of the total liquid weight per minute. With this temperature cycle, the bar is dried in less than 20 minutes. This allowed saturated samples to be placed directly into a furnace and sintered to theoretical density all in one step. Eliminating the need for a separate drying and/or burnout cycle would significantly improve processing rates and production costs.

All evidence suggests that the lack of shrinkage during drying is due to the high relative density achieved during isopressing. Namely, the particles are pushed into elastic contact during isopressing, and the capillary pressure produced during evaporative drying is too small to further rearrange the particles. Uniform shrinkage and the absence of either shape distortion or cracking were found after sintering of alumina pieces at 1500°C for 2 hours. This is indicative of uniform particle packing throughout the bodies; otherwise less dense regions would exhibit greater shrinkage during densification, leading to warping. By reducing any shape changes during post-forming processes, machining of dense components is minimized or eliminated altogether.

Colloidal Isopressing of ceramic powders has been introduced as a new method to form ceramic components from colloidal suspensions. The method starts with a slurry that can be filtered to remove strength degrading inclusions. After an initial, low pressure consolidation to create a fluid-like consolidated body, the shape forming method requires only a short isopressure period within the mold. Following shaping, the saturated body can be rapidly dried without shrinkage, or in the present case, heated directly to the densification temperature. Post-processing machining is minimized or eliminated because the shape and contours imparted by the mold are retained during drying and densification. As will be reported later, the versatility of the process has been demonstrated for zirconia and silicon nitride aqueous slurries, where the short-range repulsive potential is developed by steric methods. Finally, the implementation of Colloidal Isopressing does not require the development of new capital equipment: filter (de-watering) presses are used in the clay industry to consolidate clay slurries, and isostatic presses are used to produce millions of spark plug insulators daily.

References

- 1 F. F. Lange, "Powder processing science and technology for increased reliability," *J. Am. Ceram. Soc.* **72**, 3 (1989).
- 2 R. E. Mistler, D. J. Shanefield, R. B. Runk, "Tape casting of ceramics," in *Ceramic Processing Before Firing*, G. Y. Onoda, L. L. Hench, Eds. (Wiley-Interscience, New York, 1978) pp.411-448.
- 3 J. S. Reed, in *Principles of Ceramic Processing* (Wiley-Interscience, New York, ed. 2, 1995) pp. 493-503.

- 4 F. F. Lange, K. T. Miller, "Pressure filtration: Consolidation kinetics and mechanics," Am. Ceram. Soc. Bull. **66**, 1498 (1987).
- 5 J. A. Mangels, "Injection molding ceramics," Ceram. Eng. Sci. **3**, 529 (1982).
- 6 A. C. Young, O. O. Omatete, M. A. Janney, P. A. Menchhofer, "Gelcasting of alumina," J. Am. Ceram. Soc. **74**, 612 (1991).
- 7 T. J. Graule, F. H. Baader, L. J. Gauckler, "Shaping of ceramic green compacts direct from suspensions by enzyme catalyzed reactions," cfi/Ber. DKG **71**, 317 (1994).
- 8 G. V. Franks, B. V. Velamakanni, F. F. Lange, "VibraForming and in-situ flocculation of consolidated, coagulated alumina slurries," J. Am. Ceram. Soc. **78**, 1324 (1995).
- 9 G. W. Scherer, "Theory of drying," J. Am. Ceram. Soc. **73**, 3 (1990).
- 10 V. K. Pujari et al., "Reliable ceramics for advanced heat engines," Am. Ceram. Soc. Bull. **74**, 86 (April 1995).
- 11 G. V. Franks, F. F. Lange, "Plastic-to-brittle transition of saturated, alumina powder compacts," J. Am. Ceram. Soc. **79**, 3161 (1996).
- 12 J. C. Chang, F. F. Lange, D. S. Pearson, J. P. Pollinger, "Pressure sensitivity for particle packing of aqueous Al_2O_3 slurries vs. interparticle potential," J. Am. Ceram. Soc. **77**, 1357 (1994).
- 13 R. G. Horn, "Surface forces and their action in ceramic materials," J. Am. Ceram. Soc. **73**, 1117 (1990).
- 14 D. C. C. Lam, K. Kusakari, "Microstructure and mechanical properties relations for green bodies compacted from spray dried granules," J. Mater. Sci. **30**, 5495 (1995).

Material System	Relative Density after Consolidation at 5MPa	Relative Density after Isopressing at 300MPa
Alumina		
AKP-50, 0.24 μm pH 4, 0.5M NH_4Cl	57%	62%
AKP-30, 0.40 μm pH 4, 0.5M NH_4Cl	58%	64%
AKP-15, 0.65 μm pH 4, 0.5M NH_4Cl	58%	64%

Table 1: Relative densities, for 3 alumina powders with different particle size, before and after isopressing at 300MPa for 5 minutes. The error in these values is approximately $\pm 1\%$

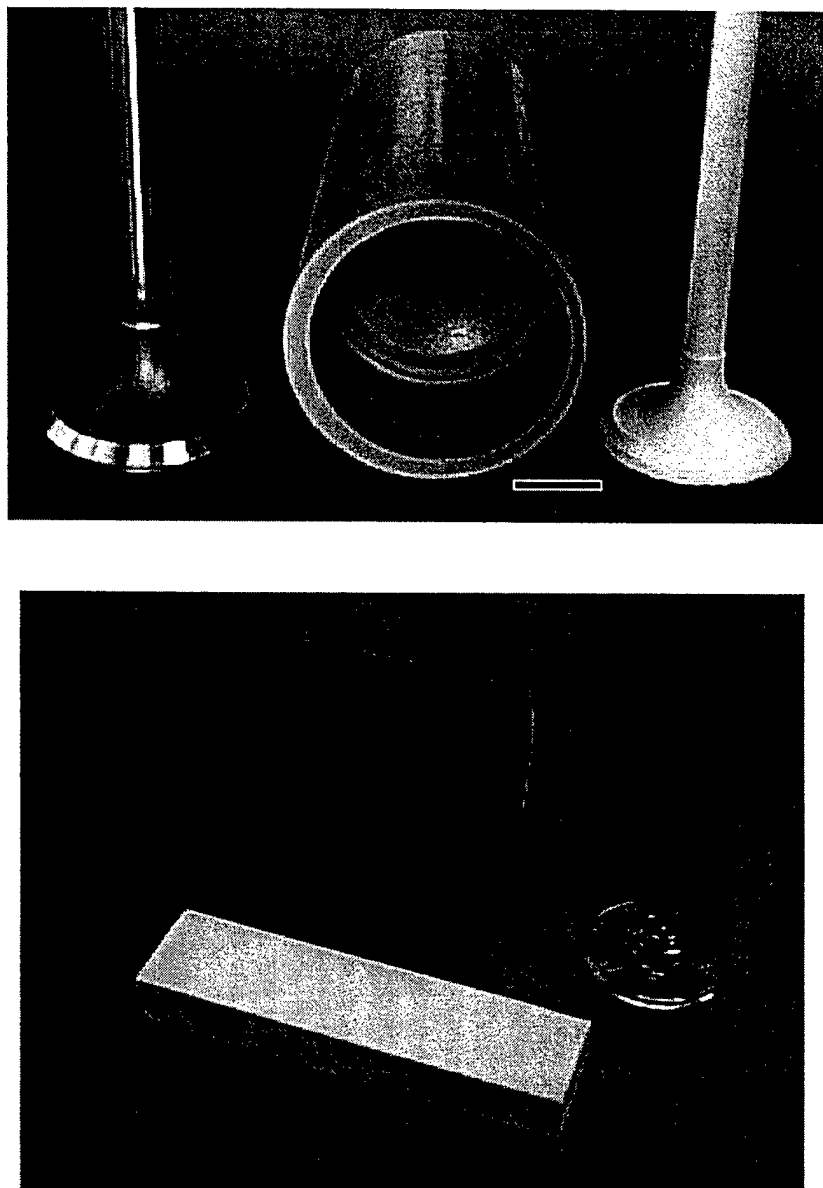


Figure 1: Examples of isopressed components from AKP-50 alumina. (a) Metal engine valve (left), silicone rubber mold cast from the metal part (center), and sintered alumina valve (right). (b) Green, dried bar formed in the pictured silicone mold; this is typical of the components used for mechanical characterization.

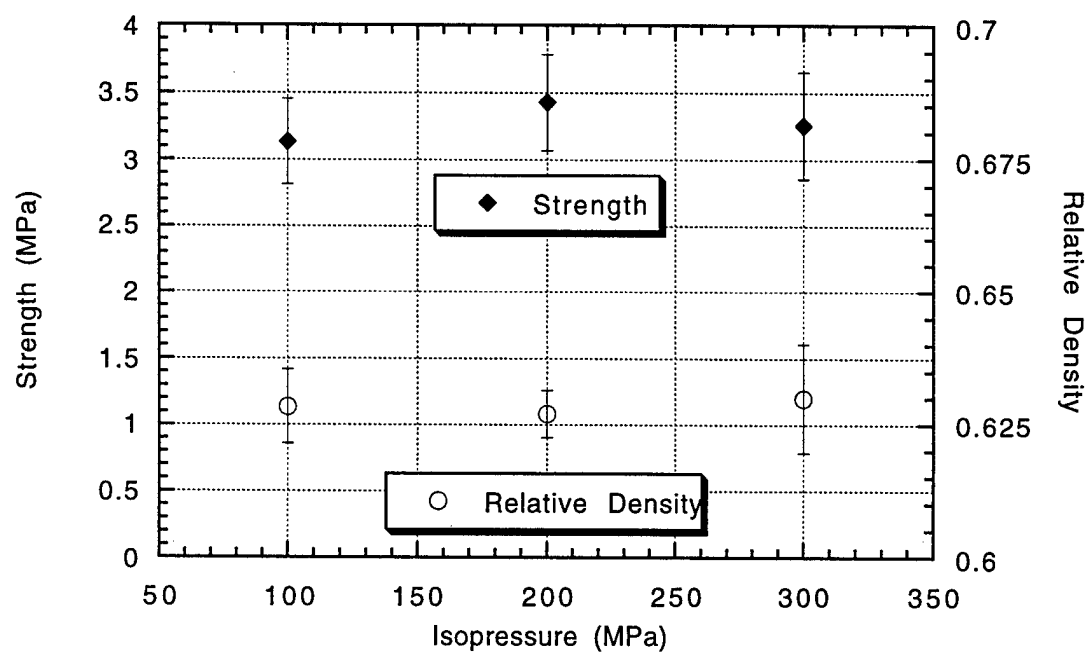


Figure 2: 3-point bending strength and relative density of compacts at various applied isopressure for AKP-50 ($0.24\ \mu\text{m}$) alumina at $0.5\text{M NH}_4\text{Cl}$, and pre-consolidated at 5MPa .

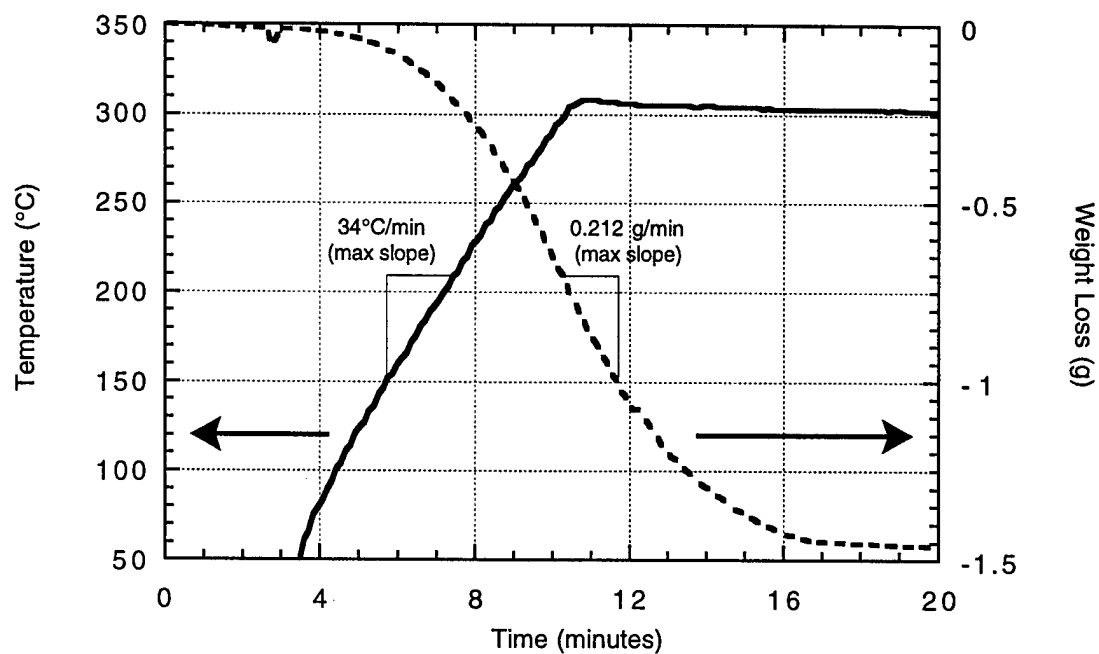


Figure 3: TGA measurement on drying of an isopressed bar using a heating rate of 30°C per minute up to 300°C. All of the liquid in the bar is removed in less than 20 minutes without any damage.

Technical Report # 5

January 25, 2001

Contract Number: DAAG55-98-1-0455

send to J. Am. Cerm. Soc.

Compact Formation During Colloidal Isopressing

Benjamin C. Yu, P. Maarten Biesheuvel, and F. F. Lange
Materials Department, University of California
Santa Barbara, CA 93106

Abstract

In Colloidal Isopressing, a consolidated, fluid-like body with a high relative density (e.g., 0.58) is converted into an elastic body under the influence of an isostatic pressure. Experiments show that during isopressing a sharp transition plane exists between the fluid-like and elastic portions of the iso-pressed compact, where the size of the elastic fraction increases with time. The elastic portion is formed against a piece of porous material in a rubber mold; the porous material will accommodate the liquid phase squeezed out of the fluid-like body, allowing for the conversion to a denser elastic body (0.63). The results of experiments with varied isopressure are compared with simulations based on a filtration model. The good agreement indicates that Colloidal Isopressing can be considered a special case of consolidation via pressure filtration. Compared to conventional consolidation via pressure filtration, the extremely rapid consolidation period is due to the large relative density of the fluid-like body used to fill the mold and the high iso-pressure. The simulation used here is a useful tool in the design and understanding of shape forming by Colloidal Isopressing and clearly shows how process variables such as particle size, initial relative density and applied pressure influence the minimum required to form the elastic body.

Introduction

Yu and Lange have recently introduced a new shape forming method for ceramic slurries called Colloidal Isopressing. [1] This method begins with a relatively dilute, dispersed slurry (e.g., volume fraction of $\phi \sim 0.20$) that can be passed through a filter to eliminate inhomogeneities greater than a given size (i.e. foreign particles, hard agglomerates, etc.) from the powder. As explained by Lange [2] and demonstrated by Pujari *et al.* [3] with silicon nitride powder, it is possible to significantly improve the reliability of ceramic components by removing strength degrading flaws by a simple filtration step. After filtration, the slurry is reformulated so that the powder forms a weakly attractive particle network. In this state, the particles sit in a shallow potential well, separated from touching one another at an equilibrium distance. The weakly attractive network has several important roles in processing. First, it prevents mass segregation due to sedimentation.[4] Second, the short-range repulsive potential that is responsible for the weakly attractive network allows the slurry to be concentrated by pressure filtration to form a plastic body with a high volume fraction of powder ($\phi \sim 58\%$). If the

In the present work we will combine equations (3), (5) and (7) from Biesheuvel and Verweij [7] to describe the compact growth velocity by:

$$\frac{d\delta_c}{dt} = \frac{\phi_p}{\phi_c - \phi_p} \frac{L_c P_c}{\eta \delta_c} \quad (1)$$

Here, δ_c [m] is the compact thickness, t [s] the time, ϕ_c and ϕ_p [-] the compact and fluid-body particle volume concentration, L_c [m²] the permeability of the consolidated body, P_c [Pa] the pressure difference between the top and bottom of the consolidated body, and η [Pa·s] the liquid (or filtrate) viscosity. The assumptions used to derive equation (1) include: 1) The liquid and the particles are incompressible, thus their mass densities are independent of pressure. 2) The compact does not densify either in time or with place, as is generally the case for dispersed particles, [6,8] though not necessarily true for coagulated systems [9,10] – we will return to this issue later. 3) Filtration is one-dimensional and planar. 4) The pressure exerted by the isostatic press overrules all other driving forces, such as gravity, the capillary forces in the filter, and the elasticity of the elastomer mold. 5) The filter has sufficient void volume to accommodate all of the liquid required to convert the fluid-body into the consolidated body, and the pressure of the gas within the filter, compressed during filtration, can be neglected.

It is the pressure differential over the consolidated body, P_c , that drives the fluid through to the filter. Because the filter exhibits resistance to the flow of liquid into it, P_c will be lower than the externally applied pressure, P_e , by:

$$P_c = P_e - P_f \quad (2)$$

where P_f is the back-pressure produced by the filter. P_f must be determined by understanding the distance the liquid flows into the filter material, δ_f , as a function of time:

$$\delta_f = \frac{\delta_w}{1 - \phi_f}, \quad (3)$$

where δ_w ($= H_0 - H$) is the change in thickness of the entire body, $(1 - \phi_f)$ is the volume fraction of void phase in the filter, and δ_w is related to δ_c by:

$$\delta_c = \delta_w \frac{\phi_p}{\phi_c - \phi_p} \quad (4)$$

The ratio of P_c to P_f is given by

$$\frac{P_c}{P_f} = \frac{\delta_c L_f}{\delta_f L_c}, \quad (5)$$

where L_f and L_c are the permeabilities of the filter and compact, respectively. By combining equations (2)-(5), one can determine P_c as function of P_e :

$$P_c = P_e \left\{ 1 + \frac{L_c (\phi_c - \phi_p)}{L_f (1 - \phi_f) \phi_p} \right\}^{-1} = P_e \cdot \xi \quad (6)$$

where ξ is the correction factor relating P_c to P_e .

To determine the time required to fully consolidate the body within the rubber cavity, equation (1) must be integrated with knowledge of how P_e changes with time. For Colloidal Isopressing, it is assumed that P_e has three linear periods as shown in Figure 2. The first period

(I) is up-loading at a ramp rate of α (Pa/s), the second period (II) is a hold at the maximum pressure, $P_{e,m}$, for a defined period, and the third period (III) is unloading at a ramp rate of β .

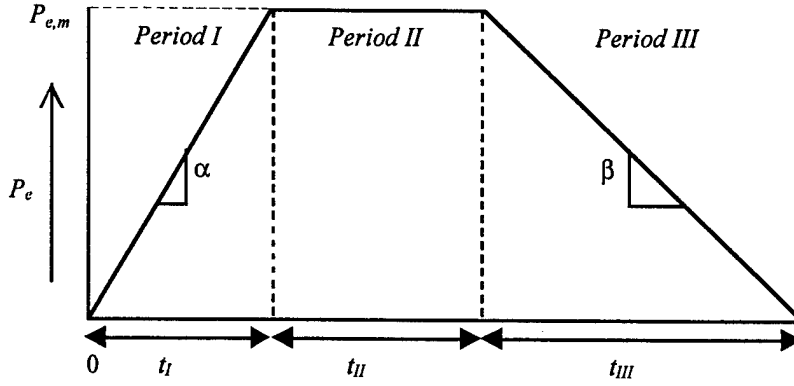


Figure 2. External pressure P_e change during consolidation. Period I is characterized by an upward ramp rate α (Pa/s), period II by the time for which the maximum pressure $P_{e,m}$ is maintained, and period III by the downward ramp rate β .

For the first period,

$$P_e(t) = \frac{P_{e,m}}{t_I} \cdot t = \alpha \cdot t \quad (7)$$

Combining equations (6) and (7), the integration of equation (1) with boundary conditions $\delta_c|_{t=0} = 0$ and $\delta_c|_{t=t_I} = \delta_{c,I}$ results in a compact thickness, at the end of period I, of:

$$\delta_{c,I} = \sqrt{\frac{\phi_p L_c \alpha \xi}{(\phi_c - \phi_p) \eta}} \cdot t_I \quad (8)$$

For the constant pressure period, $P_e = P_{e,m}$, the integration of equation (1) with the boundary conditions $\delta_c|_{t=0} = \delta_{c,I}$ and $\delta_c|_{t=t_{II}} = \delta_{c,II}$ results in:

$$\delta_{c,II} = \sqrt{\frac{2\phi_p L_c \xi P_{e,m} t_{II}}{(\phi_c - \phi_p) \eta}} + \delta_{c,I} \quad (9)$$

During the third period,

$$P_e(t) = P_{e,m} - \beta \cdot t \quad (10)$$

and with the boundary conditions, $\delta_c|_{t=0} = \delta_{c,II}$ and $\delta_c|_{t=t_{III}} = \delta_{c,III}$, integration of equation (1) using (6) and (10) gives:

$$\delta_{c,III} = \sqrt{\frac{2\phi_p L_c \xi}{(\phi_c - \phi_p) \eta} (P_{e,m} t_{III} - \frac{1}{2} \beta t_{III}^2)} + \delta_{c,II} \quad (11)$$

Now, we can determine the total thickness ($\delta_{c,t} \equiv \delta_{c,III}$) of the compact after the three periods by combining equations (8), (9) and (11):

$$\delta_{c,t} = \sqrt{\frac{\phi_p L_c \xi P_{e,m}}{(\phi_c - \phi_p) \eta} [2t_{II} + P_{e,m} (\alpha^{-1} + \beta^{-1})]} \quad (12)$$

The above equations are most useful to experimentally examine consolidation phenomena during isopressing. For implementation of Colloidal Isopressing, it is important to predict the total time, t_t , required to convert a given length of consolidated slurry into an elastic body. Prior to isopressing, the entire length of consolidated slurry in the mold is H_0 . This is related to the final compact thickness by:

$$H_0 = \delta_{c,t} \frac{\phi_c}{\phi_p} \quad (13)$$

Therefore, if we combine equations (12) and (13), and add the times required for the isopressure ramps up and down, we find that:

$$t_t = \frac{\phi_p(\phi_c - \phi_p)\eta}{2\phi_c^2 L_c} \frac{H_0^2}{\xi P_{e,m}} + \frac{P_{e,m}}{2} (\alpha^{-1} + \beta^{-1}) \quad (14)$$

A conservative estimate of the time can be calculated by neglecting the ramping periods, and thus only accounting for the period of constant applied pressure. In addition, if we also neglect the resistance to liquid flow in the filter ($\xi = 1$) then we may simplify equation (14) to:

$$t_{hold, approx} = \frac{(\phi_c - \phi_p)\eta}{2\phi_p L_c P_{e,m}} \delta_{c,t}^2 \quad (15)$$

It is interesting to note that this is the same relationship derived by Lange and Miller [6] for conventional pressure filtration.

In the above equations, one either needs to determine the permeability of the consolidated body and the filter through experiments, or by calculation using the Carman-Kozeny equation:[11]

$$L = \frac{(1 - \phi_c)^3}{180\phi_c^2} \left(\sum_{j=1}^m \frac{f_j}{d_j} \right)^{-2}, \quad (16)$$

where the size distribution of the powder is given by m particle fractions with sizes d_j and fraction f_j , which is the volume fraction associated with particle type j ($\sum_{j=1}^m f_j = 1$).

Experimental

A dispersed slurry containing 0.20 volume fraction of α -alumina (Sumitomo Chemical Co., Grade AKP-50) with an average particle size of 0.25 μm was prepared in distilled water, at pH 4 using nitric acid. Ultrasound (Heat Systems-Ultrasonics, Inc., Sonicator W-380) was applied during mixing to break up agglomerates. NH_4Cl salt (Fisher Chemical, Analytical Grade) was added, 0.5M based on the volume of water, while maintaining a pH of 4 with nitric acid to produce a weakly attractive particle network. [12] The slurry was bottled and allowed to equilibrate for at least 24 hours prior to use, while rolling to maintain agitation. All slurries were processed within one week of their initial preparation.

The alumina suspensions were pre-consolidated by uniaxial pressure filtration [6] to increase the volume fraction of solids prior to isostatic compaction. A pressure of 5 MPa was applied until the plunger stopped moving for a minimum of 15 minutes. At this point it was assumed that the particle network within the die was completely supporting the applied pressure.

After pressure filtration, the relative density of the powder in the saturated compact was 0.58 ± 0.01 , in good agreement with previously reported values by Franks and Lange [5].

The relative densities, determined for saturated powder bodies in this work, were calculated by the weight loss method. Bodies were weighed immediately after processing to determine the saturated weight with minimal evaporation. Samples were then dried at 70°C for at least 24 hours, and heated to 500°C for 3 hours to determine the weight loss due to water and salt, respectively. The relative density of each body was then calculated from the weight changes and the densities for water (1.0 g/cc), NH_4Cl (1.5 g/cc), and Al_2O_3 (3.98 g/cc).

The filter-pressed bodies were transferred to a plastic bag and any touching particle network formed during the pre-consolidation stage was easily broken apart by vibration (Cleveland Vibrator Co., Inc., Model CM-30). The resulting consolidated slurry could easily be made to flow. It exhibited a slight dilatant behavior due to the high solids loading, and had a consistency similar to toothpaste. The fluid-like consolidated body was then transferred to a syringe and extruded by hand into the isopressing die cavity.

Silicone rubber die cavities (General Electric Co., Grade RTV 644A) were made by casting around a machined metal bar with a cross-sectional dimension of 12.7×6.4 mm, and a length of about 120 mm. The porosity required to accommodate the liquid squeezed out during Colloidal Isopressing was provided for by placing a partially sintered, AKP-15 alumina piece (average particle size $0.65 \mu\text{m}$), 23.2 mm in length, at one end of the die cavity. The porosity of the partially sintered alumina filter was determined to be about 35%. It is assumed that the change in air volume in the filter, due to the influx of liquid during isopressing, does not create enough pressure to affect the process. Typically, the die cavity is filled with about 60 mm of consolidated slurry, which loses about 3.4 volume percent of water during isopressing. The air volume in the filter, consequently, will decrease by $(60 \times 3.4\%) / (23 \times 35\%) \times 100\% \approx 25\%$, which means the air pressure in the filter will increase, according to the ideal gas law, to 134 kPa (from 100 kPa). Clearly, this increase in air pressure within the filter will have no influence on the total driving force, which is on the order of 100 MPa.

The filter material was separated from the paste by a piece of Teflon filter paper. After injecting the consolidated slurry into the mold, the entire mold was sealed and bagged for isostatic pressing in a cold isostatic press (Autoclave Engineers, Inc., Model IP-2-22-60). The isopressing experiments were carried out with a constant up-loading ramp rate ($\alpha \approx 7.76 \text{ MPa/s}$), a constant down-loading ramp rate ($\beta \approx 2.47 \text{ MPa/s}$), and a constant hold time (t_H) of 10 seconds at the maximum pressure, $P_{e,m}$. In different experiments, the maximum external pressure ($P_{e,m}$) was varied from 60 to 100 MPa.

After isopressing, the bodies were slowly pushed out of the cavity (demolding step) with the fluid-like end emerging first. Pieces were cut off as they emerged from the mold such that the entire body was cut into parallel slices. Each piece was immediately weighed in its saturated state. These slices were subsequently dried at 70°C and heated to 500°C to determine the relative density of each slice, using the weight difference method. The relative density was plotted as a function of the distance from the filter/body interface to help determine the development of the compact over time.

In the partially isopressed bodies, there exists a slice that has an intermediate relative density, ϕ_i , an average of the consolidated slurry and the dense compact: $\phi_i = (\phi_c + \phi_p)/2$. We assume that this piece contains the compact/consolidated slurry interface. From the weight of each slice, its density, and the cavity cross section, we calculate the distance for the cut closer to

the filter (x_1) and further from the filter (x_2) that surround the piece at ϕ_f . We then estimate the compact size to be at the center of this piece:

$$\delta_{c,t} = \frac{x_1 + x_2}{2} \quad (17)$$

Results

The sliced, dried and heated specimens isopressed at $P_{e,m} = 60, 80$ and 100 MPa ($\alpha = 7.76$ MPa, $\beta = 2.47$ MPa, constant pressure hold period = 10 s) are illustrated in Fig. 3. As shown, the portions to the left are still fluid-like, whereas portions to the right, i.e. those nearer to the filter, have become elastic and retain the shape of the mold. Note that the mold design requires that the sample be pushed out in the longitudinal direction. Because the untransformed end emerged first, the compact section had to travel through the portion of the mold with the consolidated slurry. This fluid-like material may have left a thin coating on some pieces of the compact. Any minor affect this may have had on the measured relative densities was ignored.

Figure 4 shows the relative densities for the different slices, as a function of distance from the filter, of four different samples, formed at 60, 80, 93 and 100 MPa. Prior to isopressing, the relative density of the fluid-like consolidated body was $\sim 0.586 \pm 0.003$. After isopressing, pieces nearest the body/filter interface had an average relative density (ϕ_c) of $\sim 0.626 \pm 0.005$. The slices furthest from the filter, which are still plastic, had a relative density (ϕ_p) of $\sim 0.589 \pm 0.005$. From these values, we calculate the intermediate relative density, ϕ_f , as 0.606. Using the slice with relative density nearest to ϕ_f , we apply equation (17) to determine the compact size after isopressing; this is plotted as a function of applied isopressure in Figure 5. The solid line in this figure was calculated from equation (12) and using data from Table 1. Only the compact permeability, L_c , was adjusted to achieve the fit to the experimental data.

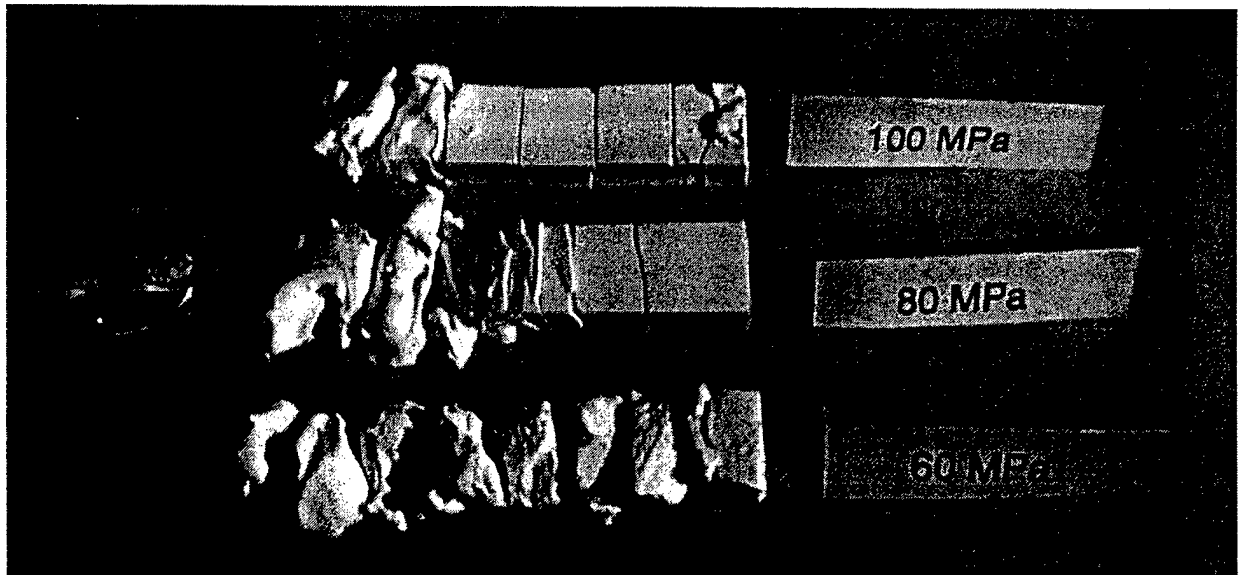


Figure 3. Three samples partially formed by Colloidal Isopressing and sliced into pieces. The filter was located on the right of each bar.

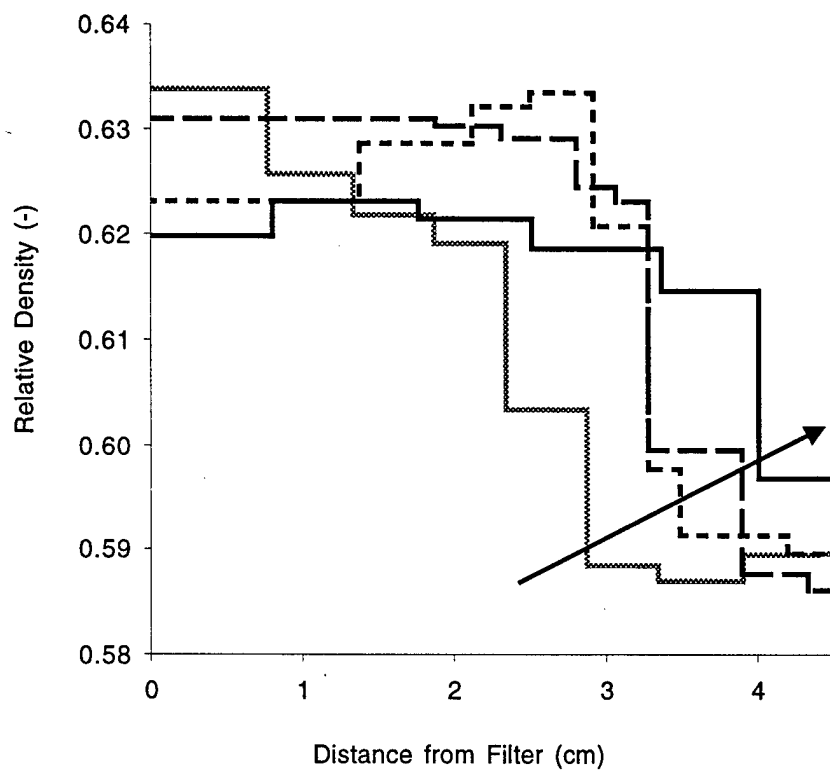


Figure 4. Relative density as function of distance from the filter/body interface. The figure shows four different samples isopressed at 60, 80, 93 and 100 MPa. The relative density of the fluid-like consolidated body used to fill the rubber die was about 0.586.

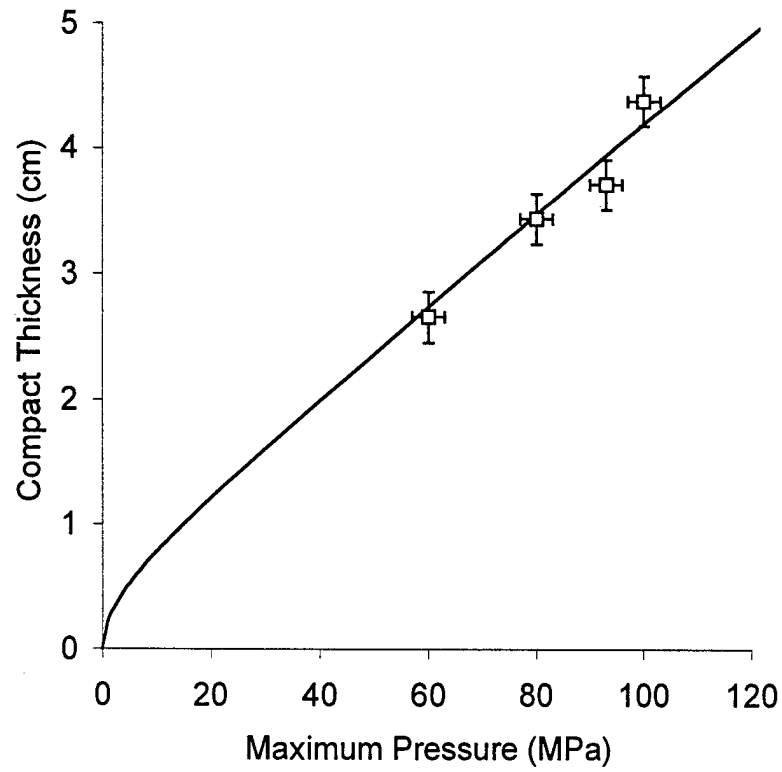


Figure 5. Length of the elastic portion of the isopressed specimens compared with calculations (equation (12)). The data for this calculation is presented in

Table 1. Only permeability, L_v , is determined to fit the experimental data.

Discussion

The specimens isopressed between 60 and 100 MPa show only a partial transformation. As illustrated in Figures 3 and 4, the elastic portion of the compacts initiate against the filter and grow into the pre-consolidated, fluid-like body. Because the relative density of the fluid-like body that is extruded into the mold (0.586) is nearly equal to the average relative density for the plastic material remaining in the mold after isopressing (0.589), we believe this material has not changed during isopressing. This behavior is precisely what has been observed in pressure filtration, i.e., the particulate compact grows against the filter, into the slurry that does not change its particle concentration.

The elastic portions of the isopressed bodies had an average value of 0.626. This value is identical to those measured by Yu and Lange for AKP-50 bodies isopressed between 100 to 300 MPa for 5 minutes. [1] This indicates that the partially consolidated bodies in this study obtain their maximum packing configuration as the densification front move away from the filter. Additionally, the packing structure does not change as the pressure is increased up to 300 MPa. The primary advantage of using such high pressures is to increase the driving force for filtration (P_c) and, therefore, reduce the time required for complete compact formation.

The compact thickness, when plotted as a function of increasing applied isostatic pressure, shows an advancing consolidation front as expect for pressure filtration (Figure 5). This is illustrated visually in Figure 3. If equation (12) were plotted using the compact permeability (L_c) as calculated by equation (16) for AKP-50, the curve would lie above the experimentally determined points. However, by reducing L_c by a factor of ~ 4 to $1.34 \cdot 10^{-17} \text{ m}^2$, we find that the curve predicted by equation (12) fits the data very well. This discrepancy has been noted previously for submicrometer particles: Biesheuvel and Verweij have measured the permeability of AKP-15 to be ~ 4 times lower than determined by the Carman-Kozeny equation. They attributed this to the roughness of the aspherical particles (increasing the surface area) and presence of fines (clogging interstices between larger particles), both of which would impede flow through the powder compact. In the present case, the applied isopressure during the filtration process is also expected to compress the Hertizan powder compact. This would lead to a smaller pore size between particles, reducing the permeability of the compact.

The data used for the calculations are listed in Table 1. Note that ξ (see equation (6)) is near unity (namely 0.99 when we use the fitted value for L_c). This shows that the mold resistance is negligible because the larger particles comprising the filter will have larger interstices than in the compact (AKP-15 particle diameter of $\sim 0.65 \text{ }\mu\text{m}$ for the filter vs. AKP-50 of $\sim 0.25 \text{ }\mu\text{m}$ for the compact). Additionally, the penetration depth of liquid into the filter is very low: while the cast will grow to $\sim 60 \text{ mm}$ (given enough time), the penetration of liquid into the filter would only).

Table 1. Experimental data and values used in simulations.

Liquid viscosity η	$8.9 \cdot 10^{-4}$ Pa.s
Compact packing factor ϕ_c	0.626
Paste packing factor ϕ_p	0.589
Packing factor of the filter ϕ_f	0.65
Fitted permeability for the compact L_c	$1.34 \cdot 10^{-17}$ m ²
Calculated !! permeability of the filter L_f	$4.55 \cdot 10^{-17}$ m ²

From the measurements (and using equations (9) and (12)) we see that at 100 MPa a body of length of ~ 30 mm has formed after ~ 20 s (the end of the constant-pressure period II) and ~ 45 mm after ~ 1 min (at the end of period III). For the first 20 s, an average growth velocity of 1.5 mm/s is thus attained. This value is incredibly large compared to other filtration processes which use lower pressures (often based on the pressure difference between vacuum and atmospheric pressure, thus $P_m < 100$ kPa) and much lower slurry concentrations ($\phi_s = 0.20$ is typically considered a high loading).

In order to completely consolidate a 60 mm long body, applying equation (14) predicts a total time of ~ 103 seconds. Subtracting the ramp periods, we find the hold time (t_{II}) at 100 MPa is ~ 49 s. Alternatively, if we use the approximated time based on equation (15), where $\xi = 1$ and we ignore the ramp periods, we find that the estimated hold time is ~ 75 s at 100 MPa. However, once we add the time it takes to raise and release pressure, we find the total time by this estimate increases to ~ 128 s. This means that using the approximated time overestimates the total time (t_I) by 20%.

Conclusions

Colloidal Isopressing can be considered a filtration process. This conclusion is supported by (1) the observed fluid-like body/compact transition in a body consolidated for short periods, and (2) the agreement between predictions from a filtration model based on Darcy's law and experiments. Incidentally, this agreement demonstrates that the filtration models typically used for dispersed particles can also be applied to the coagulated system in this case.

Colloidal Isopressing combines in a new manner aspects of slip casting (a porous mold/filter is used to absorb expressed water) and pressure filtration (an externally applied pressure is the driving force). The filtration character implies that a front moves inward from the surface of any filters present within the mold cavity into the paste (for our experiments with alumina ϕ_p is typically 0.589) leaving behind a compact ($\phi_c \sim 0.626$). When used for more complex shapes, the explicit filtration equations used here will no longer describe the process quantitatively, but can still be used to understand the process in a qualitative manner. The multidimensional set of equations necessary to describe Colloidal Isopressing in complex geometries can be derived easily but are very difficult to solve.

The overall time required for complete transformation in Colloidal Isopressing is primarily determined by the dimensions of the mold, particle size, loading of the pre-consolidate, fluid-like body, final compact density, applied isostatic pressure and liquid viscosity. For the fine alumina particle suspensions studied here, the time required to form a body at 100MPa with

a length of ~ 45 mm was only ~ 1 minute, and it is expected that higher pressures will result in even shorter periods. Thus, Colloidal Isopressing may be used as a rapid technique to shape dense ceramic suspensions into rigid compacts from colloiddally processed powders

Acknowledgements

We gratefully acknowledge the support for this research from the Army Research Office, Contract Number, DAAG55-98-1-0455.

References

- 1 B.C. Yu and F.F. Lange, "Colloidal Isopressing: A new ceramic processing method", submitted to *Advanced Materials* (2000).
- 2 F.F. Lange, "Powder processing science and technology for increased reliability," *J. Am. Ceram. Soc.*, **72** [1] 3-15 (1989).
- 3 V.K. Pujari, D.M. Tracey, M.R. Foley, N.I. Paille, P.J. Pelletier, L.C. Sales, C.A. Willkens, R.L. Yeckley, "Reliable ceramics for advanced heat engines," *Am. Ceram. Soc. Bull.* **74** [4] 86-90 (1995).
- 4 J.C. Chang, B.V. Velamakanni, F.F. Lange, and D.S. Pearson, "Centrifugal consolidation of Al_2O_3 and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composite slurries vs. interparticle potentials: particle packing and mass segregation," *J. Am. Ceram. Soc.*, **74** [9] 2201-4 (1991).
- 5 G.V. Franks, F.F. Lange, "Plastic-to-brittle transition of saturated, alumina powder compacts," *J. Am. Ceram. Soc.*, **79** [12] 3161-68 (1996).
- 6 F.F. Lange and K.T. Miller, "Pressure Filtration: Consolidation Kinetics and Mechanics," *J. Amer. Ceram. Soc. Bull.*, **66** [10] 1498-1504 (1987).
- 7 P.M. Biesheuvel and H. Verweij, "Influence of suspension concentration on cast formation time during pressure filtration," *J. Eur. Ceram. Soc.*, **20** [7] 835-842 (2000).
- 8 L. Bergström, C.H. Schilling, and I.A. Aksay, "Consolidation behavior of flocculated alumina suspensions," *J. Am. Ceram. Soc.*, **75** [12] 3305-14 (1992).
- 9 G.V. Franks, M. Colic, M.L. Fisher, F.F. Lange, "Plastic-to-brittle transition of consolidated bodies: Effect of counterion size," *J. Colloid Interface Sci.*, **193** [1] 96-103 (1997).
- 10 S. Klein, M.L. Fisher, G.V. Franks, M. Colic, F.F. Lange, "Effect of the interparticle pair potential on the rheological behavior of zirconia powders: I, electrostatic double layer approach," *J. Am. Ceram. Soc.*, **83** [3] 513-517 (2000).
- 11 P.M. Biesheuvel, V. Breedveld, A.P. Higler and H. Verweij, "Graded membrane supports produced by centrifugal casting of a slightly polydisperse suspension," submitted (2000).
- 12 J.C. Chang, F.F. Lange, and D.S. Pearson, "Viscosity and yield stress of alumina slurries containing large concentrations of electrolyte," *J. Amer. Ceram. Soc.*, **77** [1] 19-26 (1994).

Technical Report # 6

January 25, 2001

Contract Number: DAAG55-98-1-0455

In press, J. Am. Ceram. Soc.

Effect of the Interparticle Pair Potential on the Rheological Behavior of Zirconia Powders: Part II - The Influence of Chem-Adsorbed Silanes

Sascha Klein, Matthew Fisher, George Franks, Miroslav Colic and Fred Lange

Materials Department
University of California, Santa Barbara
Santa Barbara, CA 93106

Abstract:

The influence of two bi-functional amino-silanes, N-(Triethoxysilylpropyl)-O-Polyethylen Oxid Urethan (PEG-silane), and N-(3-Triethoxysilylpropyl) Gluconamid (Glucol-silane) on the rheological behavior of aqueous zirconia (solid-solution with 3 mole % Y_2O_3) powder slurries and consolidated bodies was investigated. Adsorption of the silanes was determined with viscosity measurements. The influence of tetramethylammonium chloride added to dispersed slurries to produce weakly attractive particle networks, formulated with the amino-silane reacted powders was investigated. Bodies were consolidated by filtration at different applied pressures. Viscosity vs. shear rate behavior, and consolidated body rheology were determined for slurries formulated at different pH values and different salt contents. The Glucol-silane coated powder had a different isoelectric point ($pH = 8.5$) relative the unreacted and PEG-silane coated powders ($pH \approx 7$). Dispersed slurries with Newtonian behavior could be formulated for the following conditions: unreacted powder = $pH 11$, PEG-silane coated powder = $pH 10$, and Glucol-silane coated powder = $pH 6$. Bodies with the highest relative density (≈ 0.51) were produced from dispersed slurries (uncoated and coated); their relative density was nearly pressure insensitive. The relative density of consolidated bodies produced from slurries with an attractive particle network (formulated either at the isoelectric point or dispersed with added salt) was pressure sensitive. Bodies consolidated with the weakly attractive particle networks exhibited a critical relative density that separated the body's plastic and brittle behavior. The highest critical relative density (0.48) was achieved for bodies consolidated with salt added, dispersed slurries formulated with the longest amino-silane molecule, which produced the weakest attractive particle network. Bodies that exhibited a clay-like flow stress (≈ 0.1 MPa) could be formulated with the shorter amino-silane molecule, whereas the longer amino-silane molecule produced a fluid-like body without a significant yield stress.

1. Introduction

Two basic methods can be used to produce short-range, interparticle repulsive potentials. In one, the long range repulsive potential due to the electrostatic double layer can be converted into a short-range repulsive potential by adding excess salt. The added salt decreases the Debye length of the counterion cloud surrounding each particle, which shortens the distance between the particles before they become strongly repulsive. In the second, short molecules can be attached to the surface of the particles to produce steric repulsion at small interparticle potentials. In both cases, when the short-range repulsive potential is added to the pervasive, attractive van der Waals potential, the sum produces an interparticle potential that includes a potential well where particles reside at an equilibrium separation distance. This pair potential produces a weakly attractive, but non-touching particle network. Part I of this study dealt with the electrostatic double layer approach. Here we emphasize the second approach.

Bergström et al.⁵ formulated alumina slurries with adsorbed fatty acids of increasing molecular weight to show that the relative density of consolidated bodies increased with molecular weight. They estimated the depth of the potential well in these weakly attractive networks by truncating the van der Waals potential at twice the length of the fatty acid molecule. Larger molecules produced smaller potential wells and weaker particle networks.

Kramer and Lange⁶ investigated the rheological and consolidation properties of non-aqueous Si_3N_4 slurries with alcohols of increasing molecular weight. The alcohol molecules reacted with the $-\text{Si}-\text{OH}$ surface sites at $\approx 150^\circ\text{C}$ to produce water molecules and attached hydrocarbon chains. Viscosity vs. shear-rate data showed that the strength of the weakly attractive particle networks was inversely proportional to the molecular weight of the chem-adsorbed hydrocarbon chains. These slurries could be consolidated to a high relative density; the cylindrical, consolidated bodies formulated with the longer hydrocarbon chains exhibited plastic flow when placed under axial compression, whereas those formulated with the shortest chains were elastic and exhibited brittle failure.

Luther et al.⁷ and Ducker et al.⁸ formulated aqueous, alumina slurries with surfactant molecules. Less soluble, larger molecular weight surfactants appeared to coat the particles as bi-layers, with the hydrophilic head groups of one layer adsorbed to the particle, and the head groups of the second layer in contact with the water. By changing the pH it was possible to produce either repulsive or weakly attractive particle networks, but only elastic/brittle bodies could be formed during consolidation. It was argued, and observed via atomic force microscopy (AFM) measurements, that the surfactants were pushed away from the surface during consolidation⁸, due to their weak, phys-adsorbed bond. Thus, the particles within the consolidated body were strongly bonded together by the attractive van der Waals potential.

Colic et al.⁹ found that amino-silane molecules, strongly bound to Si_3N_4 surfaces, could be used to prepare aqueous Si_3N_4 slurries that could be consolidated to form plastic bodies. The $-\text{OCH}_2\text{CH}_3$ groups that terminate one end of the linear amino-silane molecule hydrolyze in water and react with the $-\text{Si}-\text{OH}$ surface sites on the Si_3N_4 particles. The other end of the molecule has a functional group that dissociates to produce a negative charge at $\text{pH} > 9$. It was postulated that when salt was added to the Si_3N_4 slurry formulated with the amino-silane, the adsorbed

polymer chains would collapse to decrease the equilibrium separation distance between the particles to form a weakly attractive particle network^{9,10}. Slurries containing counterions of various sizes were also investigated. Bodies consolidated from these slurries had a high relative density, and exhibited plastic behavior. The use of smaller ions such as Li^+ lead to higher flow stresses than larger ions such as TMA^+ and Cs^+ . Colic et al. also showed that the amino-silane coated particles were much less reactive in water than the non-coated powder.

The purpose of the current work is to use similar amino-silane molecules to formulate aqueous ZrO_2 slurries. Two different amino-silane molecules were used, one short and one long. As shown below, the shorter amino-silane molecule produced a weaker particle network and a lower flow stress for the consolidated bodies.

2. Experimental

As received ZrO_2 powder containing 3 mol% Y_2O_3 (Tosoh Corporation, Japan, TZ- 3YS) was used with a mean particle size of 0.39 μm (Microtrack Ultrafine Particlesize Analyzer, UPA 500). The zeta potential was determined (Zeta Meter 3.0, Zeta- Meter, New York, N.Y.), from pH 12 to 3, using 0.01 M TMACl as a background electrolyte.

Two amino-silane molecules, of different lengths and different endgroups were used: N-(Triethoxysilylpropyl)-O-Polyethylen Oxid Urethan with 4 to 6 $\text{CH}_2\text{CH}_2\text{O}$ units (22 carbon units long) denoted as PEG-silane and N-(3-Triethoxysilylpropyl) Gluconamid (11 carbon units long) denoted as Glucol-silane (Gelest Inc., Tullytown, PA). Slurries containing different amounts of PEG-silane were formulated by first adding the silane to the deionized water and then adding the 20 vol.% powder at pH 10 determined using tetramethyl ammonium hydroxide (TMAOH), while stirring and applying ultrasound (Sigma Chemical Company, St. Louis, MO). Without adjusting the pH, dispersed slurries containing Glucol-silane were spontaneously produced at a pH of 6. The end groups of both silanes, $\text{Si}(\text{OR})_3$, appeared to hydrolyze and react with the Zr-OH surface sites. Attractive particle networks were formulated by either adding salt (TMACl) or changing the pH to the iso-electric point ($\text{pH} = 7.0$ for PEG-silane and $\text{pH} = 8.5$ for Glucol-silane). The slurries were stored either on a roller or in a shaker for at least 24 hours prior to testing. Just before each experiment, the pH was readjusted to within ± 0.1 pH units with either HNO_3 or TMAOH.

The viscosity vs. shear rate behavior of the slurries was determined (decreasing from 1000 s^{-1} to 1 s^{-1}) with a dynamic stress rheometer (Rheometrics DSR) using a couette tool (29.5 mm in diameter, 44 mm long). Each slurry was consolidated by pressure filtration as described elsewhere¹¹ with an applied pressure between 2.5 MPa to 100 MPa. The pressure was maintained until the position of the plunger did not change for a period of 10 min. The cylindrical bodies (approximate dimensions: 2 cm high, 2.5 cm dia.) were removed from the cavity and their relative density was measured using the weight difference method (weight before and after drying). The body weight was determined immediately after pressure filtration, after drying in a 70°C oven for 48 hours and after heating the body for 3 hours at 500°C . The weight lost in the drying oven is assumed to be only due to water, while the organic salt and the silanes will be removed at 500°C .

Before placing the consolidated bodies into the dry oven, the mechanical behavior was determined while the saturated bodies were stored in plastic bags containing a small piece of

paper towel saturated with water to prevent evaporation. As previously described¹², the mechanical properties of the bodies were determined using a screw-driven mechanical testing machine (MTS Model 8562, Minneapolis, MN). An uni-axial compressive stress was applied to each body with a displacement rate of 1 mm/min until the height of the specimen was reduced by 20 % (40% in case of a second applied stress). The measured load-displacement curves were converted into plots of true stress versus engineering strain by assuming that the volume of the specimen remained constant while its height decreased.

3. Results

Figure 1 reports the zeta potential for the PEG- and Glucol-silane reacted zirconia powders. The zeta potential for the PEG- reacted zirconia ranged from 27 mV at pH = 3 to -37 mV at pH = 11 with an iso-electric point (i.e.p.) at pH = 7. The i.e.p for the Glucol-silane reacted zirconia was pH = 8.5, with larger zeta potentials at low pH. The unreacted powder had an i.e.p. at pH 7.5¹²

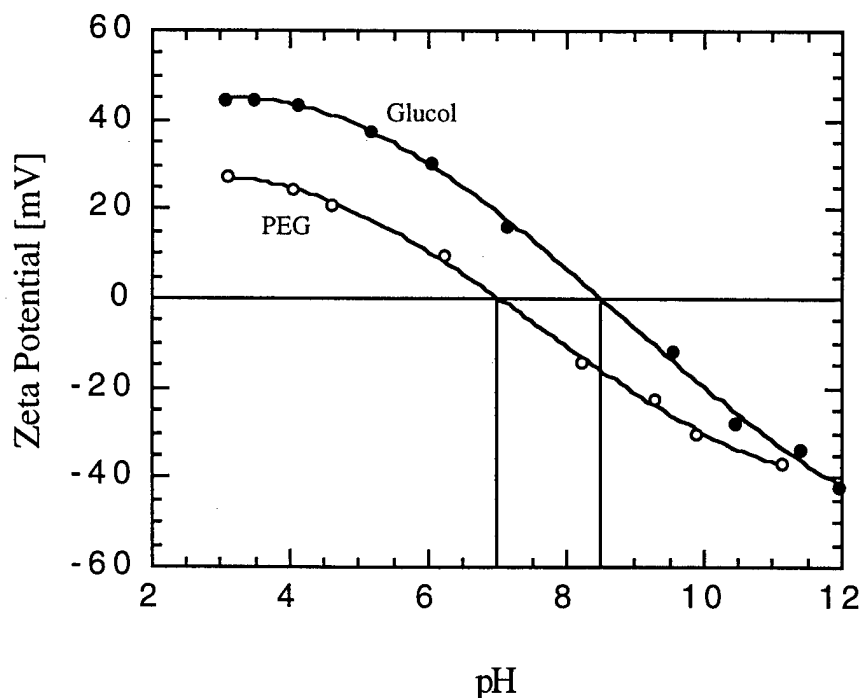


Fig. 1 Zeta potential vs. pH for the Peg- and Glucol- silane reacted zirconia powder.

Viscosity measurements were carried out for slurries formulated with different amounts of PEG- and Glucol-silane to determine the amount necessary to fully cover the surface of the powder. Figure 2 reports the viscosity of aqueous ZrO_2 slurries containing 0.5 to 3.0 weight percent PEG-silane, relative to the powder, at a pH near the i.e.p. where the viscosity was most sensitive to the added silane. As shown in Fig. 2 the minimum viscosity was observed with an addition of 1.0 wt% PEG-silane. Further additions resulted in higher viscosities apparently due to the phenomena known as depletion flocculation¹³. All other results reported below are for slurries containing 1.0 wt% PEG-silane.

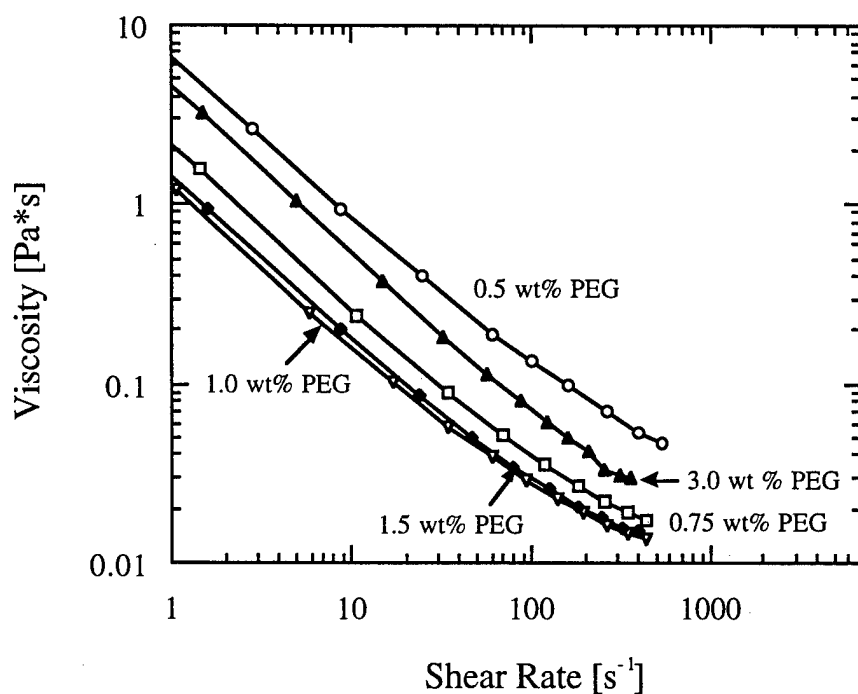


Fig. 2 Viscosity vs. shear rate plots for zirconia slurries containing different amounts of PEG-silane.

Figure 3 reports the viscosity vs. shear rate for the zirconia reacted with different amounts of Glucol-silane. The viscosity decreased up to an addition of 5 wt%. For the experiments reported below, all Glucol- slurries were prepared with 1.0 wt%.

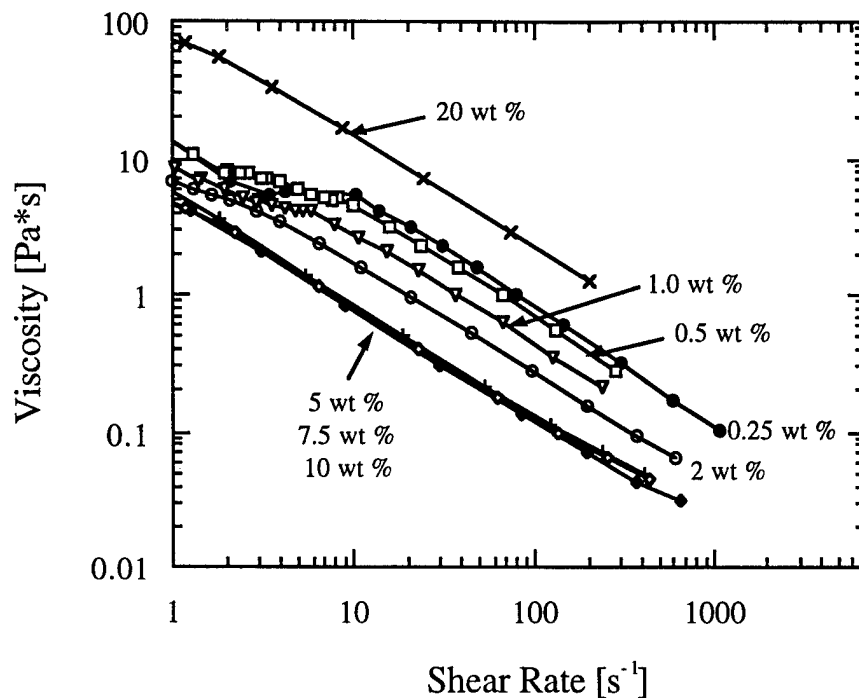


Fig. 3 Viscosity vs. shear rate for slurries with different amounts of added Glucol-silane.

Figure 4 reports the viscosity vs. shear rate data for a dispersed PEG-silane slurry ($\text{pH} = 10$), a PEG-silane slurry at its i.e.p. ($\text{pH} = 7$) and PEG-silane slurries containing 0.1 M to 1.0 M TMACl at $\text{pH} = 10$. For comparison, data is also shown for unreacted powder at $\text{pH} = 11$ (dispersed) and $\text{pH} = 7.5$ (flocced). As shown, the PEG-silane reacted powder exhibited Newtonian behavior at $\text{pH} = 10$, where it is dispersed. Either the addition of salt to the dispersed powder, or changing the pH to the i.e.p. produced attractive networks as evident by their shear-rate thinning behavior. The strongest network for slurries formulated with the PEG-silane was produced at the i.e.p. ($\text{pH} 7$). In comparison, a stronger network was produced with the unreacted powder at its i.e.p. ($\text{pH} 7.5$); its viscosity at any shear rate was an order of magnitude greater than the strongest network produced by adding salt to the reacted powder. It can also be seen that the strength of the attractive network formulated with the PEG-silane powder at $\text{pH} 10$ was dependent on the amount of added salt.

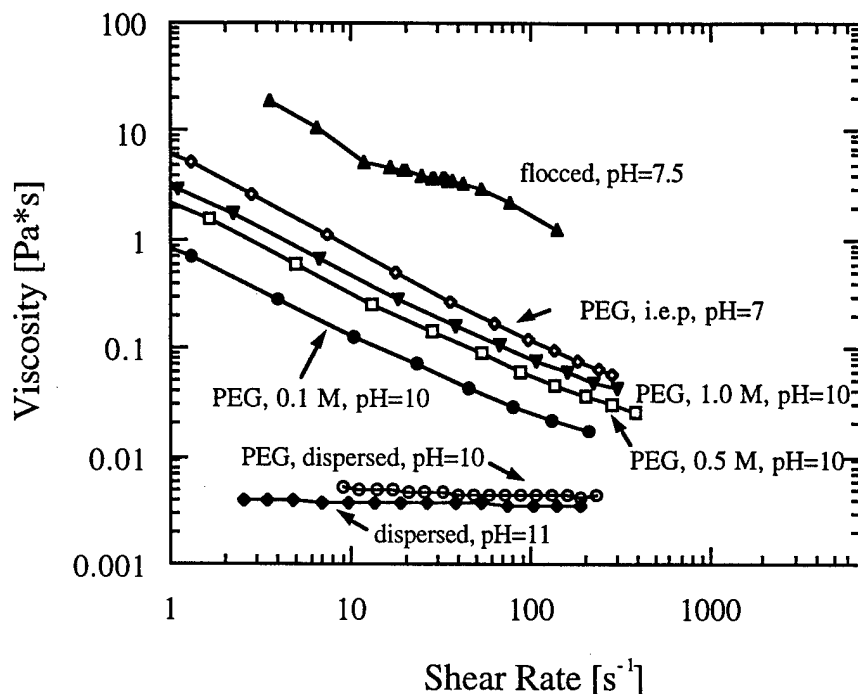


Fig. 4 Viscosity vs. shear rate plots of PEG- silane silicon nitride slurries.

The behavior of slurries containing 1.0 weight percent of the shorter Glucol- silane are shown in Fig. 5. A slurry with Newtonian behavior was not observed for the shorter Glucol-silane reacted powder at high pH values, instead, pH values of ≤ 6 were necessary to produce a low viscosity, Newtonian slurry; all other condition produced an attractive particle network. The lowest viscosities at high pH values were found at pH = 11.5. Increasing amounts of TMACl up to a concentration of 1 M, increased the strength of the attractive network produced with the addition of salt. The strongest network for the PEG-silane reacted slurries was observed at pH 8.5, the i.e.p. for this slurry.

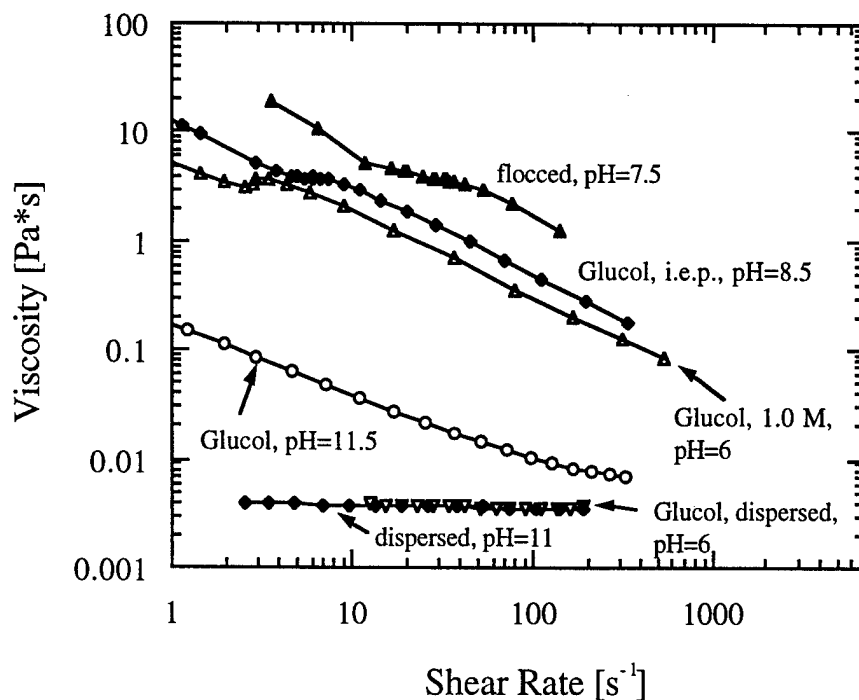


Fig. 5 Viscosity of dispersed, flocced and coagulated Glucol-silane silicon nitride slurries.

Figure 6 reports the relative density vs. consolidation pressure for bodies formed with the PEG-silane slurries; comparative data for the flocced (pH 7.5), unreacted powder is also shown¹². The dispersed slurry produced the highest relative density, between 0.49 to 0.52 over the pressure range shown. The relative density of these bodies were relatively insensitive to the applied pressure. Over the same pressure range, slurries prepared at the i.e.p. (with and without PEG-silane) produced the lowest and most pressure sensitive relative density. Comparing the two i.e.p. formulations, the one reacted with the PEG-silane exhibited a significantly higher packing density. Likewise, bodies consolidated from dispersed slurries with added salt had a relative density between the two extremes (dispersed and flocced); increased salt content produced lower relative densities.

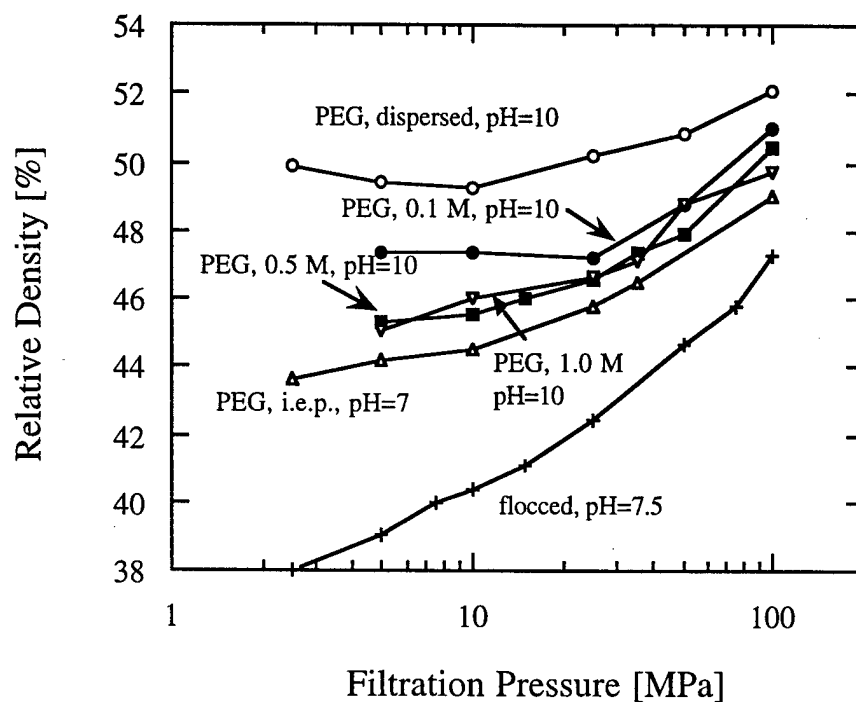


Fig. 6 Relative densities form bodies consolidated from Peg-silane silicon nitride slurries.

The relative density of powder compacts consolidated from Glucol-silane slurries are shown in Fig. 7 in comparison to the flocced bodies formed with the unreacted powder¹². Although bodies consolidated with the Glucol-silane reacted powders exhibited higher relative densities relative to bodies consolidated from unreacted powders, for comparable conditions, their relative densities were less than bodies consolidated with PEG-silane reacted powders.

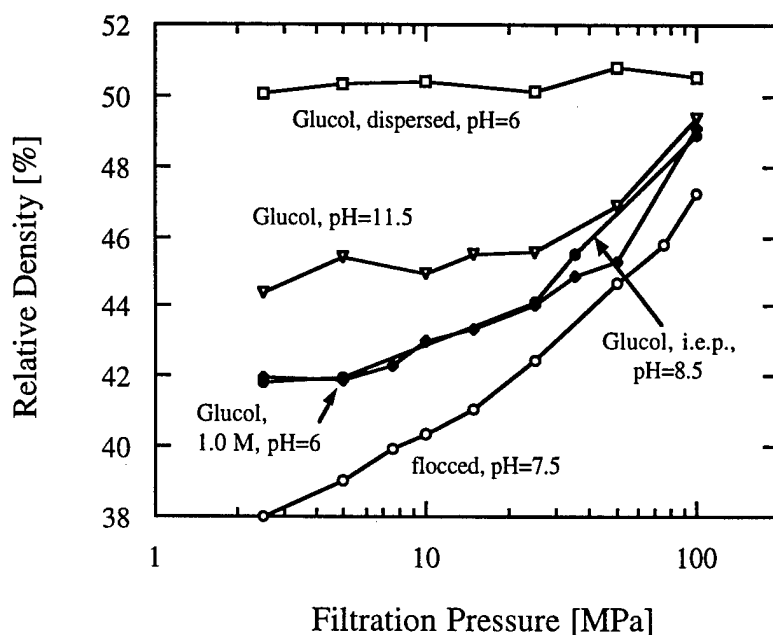


Fig. 7 Relative density vs consolidation pressure for Glucol--silane bodies.

Figure 8 shows the stress vs. strain curves for bodies consolidated from a PEG-silane slurry at its i.e.p. for consolidation pressures from 2.5 MPa to 100 MPa. In general, except for the bodies consolidated from the dispersed PEG-silane slurries, all PEG-silane compacts showed plastic behavior if they were consolidated below ≈ 35 MPa; at higher consolidation pressures, the bodies were brittle and fractured. The brittle bodies exhibit a peak stress at which they fractured, indicated in Fig. 8 with an asterisk. Plastic bodies exhibited a small peak stress followed by flow at stresses below 0.1 MPa, which can not be distinguished in Fig. 8. Figure 9 illustrates the stress-strain behavior for the same plastic bodies shown in Fig. 8 after they were loaded for a second time to a total strain of 40 %. Although the flow stresses shown in Fig. 9 are very small, they do increase with the consolidation pressure.

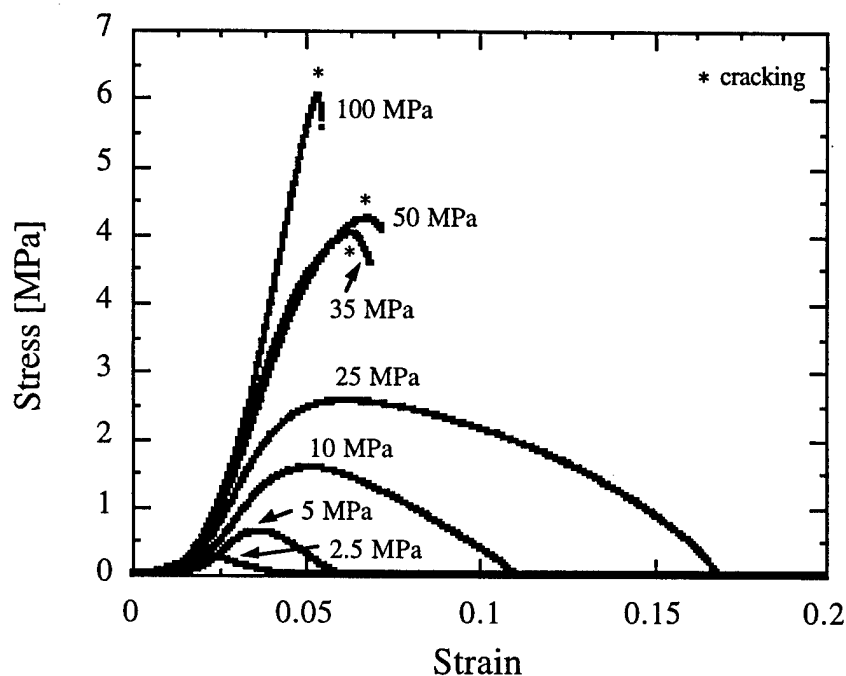


Fig. 8 Stress vs. strain plots for PEG-silane bodies consolidated at 2.5 MPa to 100 MPa.

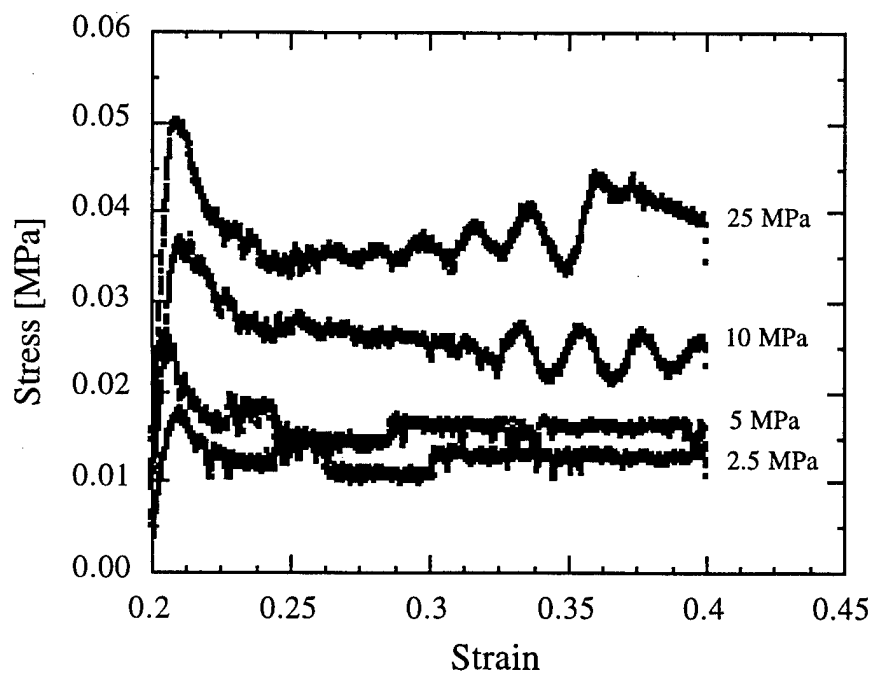


Fig. 9 Second loading of plastically deformable, PEG-silane consolidated bodies.

Stress vs. strain data for the powder compacts consolidated from the Glucol-silane slurries formulated at pH 6, containing 1.0 M TMACl are shown in Fig. 10. The plastic to brittle

transition is estimated to be between 15 MPa to 25 MPa. Bodies consolidated at 2.5 MPa and 5 MPa had a flow stress of ≈ 0.1 MPa, which is comparable to that of commercial clay¹⁴. Increasing the consolidation pressure to 7.5 MPa and 15 MPa lead to plastic samples with higher flow stresses and the formation of a broad peak before reaching a constant flow stress. Powder compacts fractured when they were consolidated at ≥ 25 MPa.

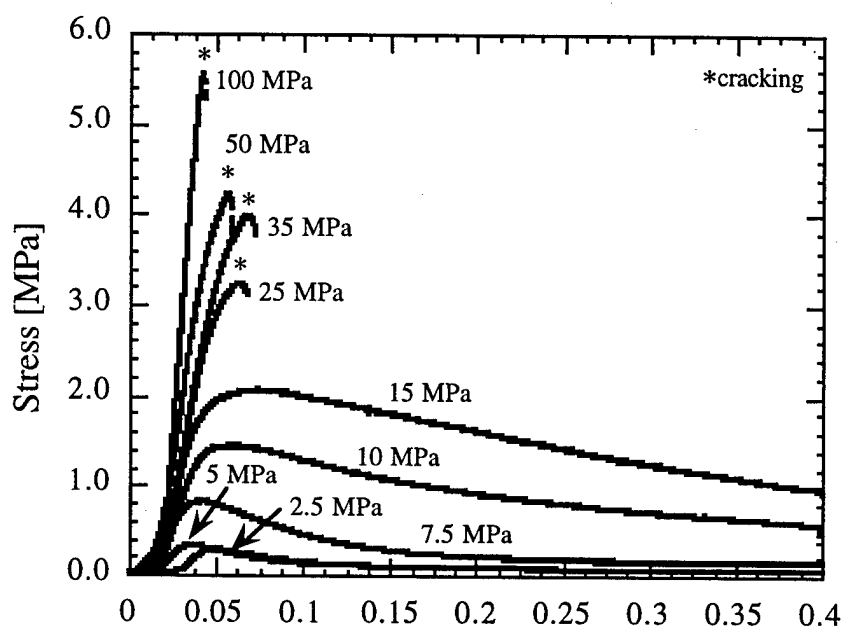


Fig. 10 Stress vs. strain data for bodies consolidated from Glucol-silane slurries formulated at pH 6 and with added 1.0 M TMACl.

Figure 11 displays the relationship between the peak stress and the relative density of the consolidated bodies. The data is presented for PEG-, Glucol-silane and, for comparison, for uncoated zirconia powder compacts. All specimens were consolidated from slurries formulated at a pH where they were dispersed and then formed into weakly attractive networks with the addition of 1.0 M TMACl. In addition, the plastic to brittle transition is indicated for each slurry system. The data shows that the plastic to brittle transition depends on the relative density as well as on the amino-silane used to coat the particles. The longer silane molecule produced the highest relative density and the highest plastic to brittle transition pressure; whereas, the unreacted powders produced a lower relative density, and a lower plastic to brittle transitions pressure.

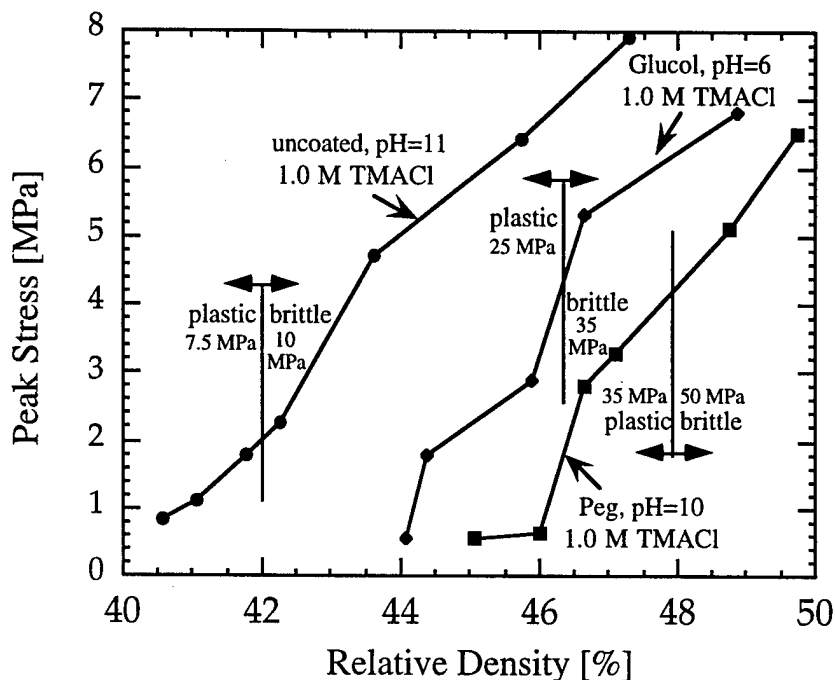


Fig. 11 Peak stress vs. relative density plots for uncoated-, Glucol- and PEG-silane powder compacts each formulated from a slurry containing 1.0 M TMACI.

The peak stress vs. relative density for uncoated-, Glucol- and Peg-silane coated powder compacts formulated of slurries at the i.e.p. and consolidated at different filtration pressure are plotted in Figure 12. The consolidation pressure for which the transition from plastic to brittle behavior occurred is also indicated for each powder type. For uncoated powder the plastic to brittle transition occurred at the lowest relative densities and at consolidation pressures between 7.5 MPa to 10 MPa. The bodies treated with PEG-silane exhibited the highest packing densities and the highest plastic to brittle transition pressures. The results for the Glucol-silane bodies were intermediate, but closer to the results produced with the PEG-silane powder compacts.

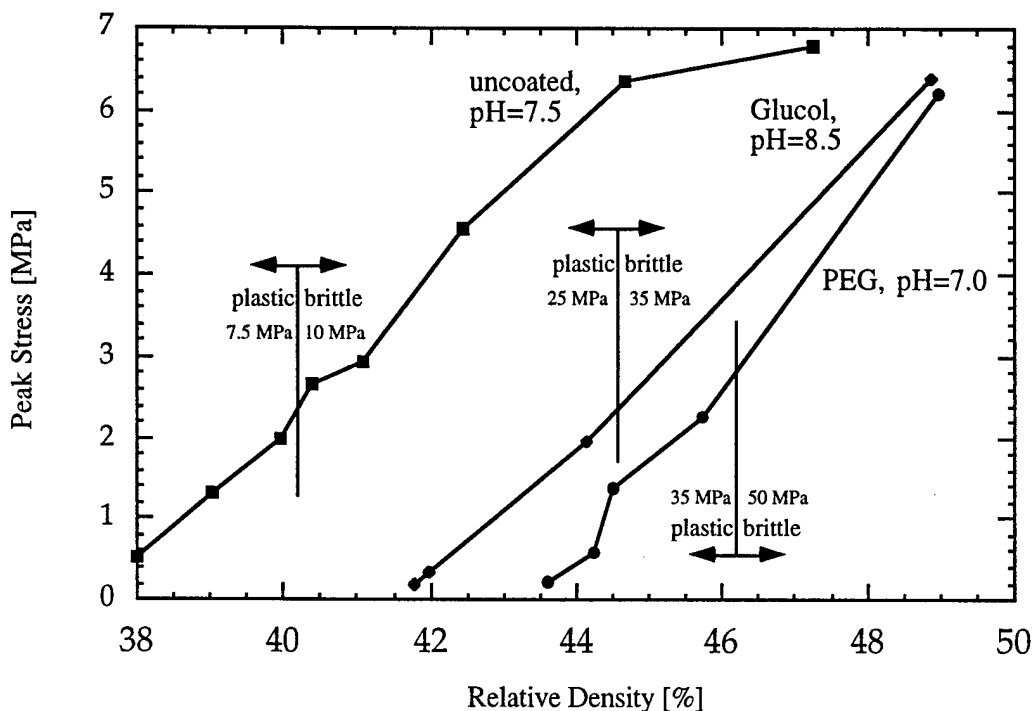


Figure 12: Peak stress vs. relative density plot for uncoated, PEG- and Glucol-silane powder compacts at the isoelectric point (i.e.p.).

4. Discussion

The major observation of the current work is that the rheological properties of both the slurry and the consolidated body depend on the length of the chem-adsorbed amino-silane molecule. The slurries made from particles coated with the longer PEG-silane molecules exhibited a lower viscosity relative to slurries prepared with the shorter Glucol-silane molecule. Likewise, while Newtonian behavior was observed for slurries formulated with the longer PEG-silane, the shorter Glucol-silane only produced attractive particle networks as evident by their shear-rate thinning behavior at high pH values. Powder compacts consolidated with slurries formulated with the longer PEG molecules packed to higher densities relative to bodies consolidated with slurries formulated with the shorter Glucol-silane molecules. The compression tests showed that the PEG-silane formulated bodies exhibited extremely low flow stresses, while the Glucol-silane bodies exhibited flow stresses comparable to those of commercial clay (0.1 MPa)¹⁵, when consolidated below the plastic to brittle transition pressure. In comparison to the rheological results found for the un-reacted powder (see Part I), slurries and their consolidated

bodies formulated with the silane molecules had lower viscosities and packed to higher relative densities.

Lea and coworkers¹⁰ reported that adding salt would collapse the very long silane chains (molecular weights of 2000 and 5000 g/mol) adsorbed on a Si_3N_4 wafer. Colic and coworkers⁹ showed that the much smaller PEG-silane, adsorbed on silicon nitride particles, can be collapsed with salt additions. In this study the PEG-silane coated ZrO_2 slurries exhibited higher viscosities with increasing salt concentration. Consistent with previous observations^{9,10}, it appears that the added salt in the current study also causes the silane molecules to collapse to decrease the particle separation distance.

Likewise, the consolidated bodies formulated with the PEG-silane powder packed to the highest densities at any given filtration pressure. Except the bodies made from dispersed PEG-silane slurries, all PEG-silane powder compacts exhibited plastic behavior. The flow stresses for the PEG- and Glucol-silane bodies were very low, compared to the bodies made with the uncoated powder. Franks and Lange¹³ show that the flow stress is related to the force needed to pull particles apart, and the number of particles per unit volume. For attractive networks, the deeper the potential well, the greater the force needed to pull the particles apart. As pointed out by Karner and Lange⁶ the shorter molecules will produce the deeper potential well. Thus, the smaller Glucol-silane molecules will produce the deeper potential well for slurries formulated with and without added salt.

The highest flow stresses observed for bodies consolidated from PEG-silane slurries are ≈ 0.05 MPa, too low for plastic forming. Bodies consolidated with Glucol-silane slurries exhibited higher flow stresses ranging from 0.1 MPa up to 1 MPa. While plastic PEG-silane bodies were extremely liquid-like despite their higher relative density, whereas the Glucol-silane compacts, with their lower relative density had a sufficient high yield stress to be plastically deformable like clay.

Acknowledgements

This research was supported by the Army Office of Research, under Grant DAAG55-98-1-0455.

References

- ¹F. F. Lange, "Powder Processing Science and Technology for Increased Reliability", *J. Am. Ceram. Soc.*, 72 [1] 3-15 (1989).
- ²R. G. Horn, "Surface Forces and Their Action in Ceramic Materials", *J. Am. Ceram. Soc.*, 73 [5] 1117-35 (1990).
- ³Pujari et al, "Reliable Ceramics for Advanced Heat Engines", *Am. Cer. Soc. Bul.*, 74 [4] 86-90 (1995).
- ⁴Y. K. Leong, P. Scales, T. W. Healy, D. Boger, and R. Buscall, "Rheological Evidence of Adsorbate-mediated Short-range Steric Forces in Concentrated Dispersions", *J. Chem. Soc. Faraday Trans.*, 89, 2473 (1993).
- ⁵L. Bergström, C. H. Schilling and I. A. Aksay, "Consolidation Behavior of Flocculated Alumina Suspensions", *J. Am. Ceram. Soc.*, 75, 3305-3314, (1992)
- ⁶T. Kramer and F. F. Lange, "Rheology and Particle Packing of Chem-and Phys-Adsorbed, Alkylated Silicon Nitride Powders", *J. Am. Ceram. Soc.*, 77, 922-928, (1994).

- ⁷E. P. Luther, T. M. Kramer, F. F. Lange, and D. S. Pearson, "Development of Short-Range Repulsive Potentials in Aqueous, Silicon Nitride Slurries", *J. Am. Ceram. Soc.*, **77** [4] 1047-51 (1994).
- ⁸W. Ducker and D. Clarke, „Controlled Modification of Silicon Nitride Interactions in Water via Zwitterionic Surfactant Adsorption“, *Colloids and Surfaces*, **99** 275-292 (1994).
- ⁹M. Colic, G. V. Franks, M. L. Fisher and F. F. Lange, „Development of Short Range Repulsive Interparticle Forces in Aqueous Si_3N_4 Slurries with Chem- Adsorbed Silanes“, submitted to *J. Am. Ceram. Soc.*
- ¹⁰A. S. Lea, J. D. Andrade and V. Hlady, „Compression of Polyethylene Glycol Chains Grafted onto Silicon Nitride Surface as measured by Scanning Force Microscopy“, *Colloids and Surfaces*, **93** 349-357 (1994).
- ¹¹K. T. Miller and F. F. Lange, "Pressure Filtration: Consolidation Kinetics and Mechanics", *Am. Ceram. Soc. Bull.*, **66** [10] 1498-504 (1987).
- ¹²S. Klein et al., "Effect of the Interparticle Pair Potential on the Rheological Behavior of Zirconia Powders: Part I - The Electrostatic Double Layer Approach", *J. Am. Ceram. Soc.*, accepted and to be published
- ¹³G. V. Franks and F. F. Lange, "Plastic-to-Brittle Transition of Saturated, Alumina Powder Compacts", *J. Am. Ceram. Soc.*, **79** [12] 3161-68 (1996).
- ¹⁴Tadros paper about Depletion Flocculation.
- ¹⁵G. V. Franks, Ph.D. Thesis, Univ. of Cal., Santa Barbara, 1997.
- ¹⁶J. Yanez, E. Laarz and L. Bergström, "Viscoelastic Properties of Particle Gels", *J. Colloid and Interface Sc.*, **209**, 162-172, 1999

Technical Report # 7

January 25, 2001

Contract Number: DAAG55-98-1-0455

Optimization of an Aqueous, Commercial Silicon Nitride Slurry for Colloidal Isopress Forming

Reto Joray,^{†,‡} Benjamin Yu,^{*,†} Fred Lange,^{*,†} and John Pollinger^{§,¶}

Materials Department, University of California, Santa Barbara, California 93106
and Ceramics Division, Allied Signal, Inc., Torrance, California, 90504

Abstract

A commercial Si_3N_4 -based aqueous slurry (AS800), was processed the enable forming shapes via a new method called Colloidal Isopressing. The as-received slurry was reformulated to contain 2 wt% PEG-silane (N-[(triethoxysilyl)propyl]-O-polyethylene oxide urethane) and 0.5 M of either tetramethylammonium chloride or tetramethylammonium nitride. The addition of the salt to an AS800 slurry formulated in the dispersed state at pH 9-10 changes the interparticle pair potential from fully repulsive to weakly attractive. Coagulated AS800 slurries were consolidated by pressure filtration at 2 MPa to a relative density of $\approx 51\%$. It was shown that the consolidated bodies could be fluidized and used to fill a rubber mold. By isopressing a specific amount of consolidated slurry contained within a rubber mold at 200 MPa for one minute, powder compacts with a relative density of ≈ 0.60 were formed with a bar shape.

Introduction

Silicon nitride-based ceramics are strong, resistant to wear, and due to their moderate elastic modulus and low thermal expansion coefficient, they are very resistant to thermal shock. Hence silicon nitride is generally the material of choice for high temperature applications. [1] Despite this unique combination of properties, components made of silicon nitride are still prone to occasional, unpredictable failure from a flaw that was present in the initial powder. One method to improve the reliability is to remove the flaw producing heterogeneities greater than a given size by passing a slurry, made from the powder, through a filter. [2] Pujari *et al.*

[†] Materials Department, University of California, Santa Barbara, California

[‡] Now at the EPFL, Lausanne, Switzerland

^{*} Member, American Ceramic Society

[§] Ceramics Division, Applied Materials, Inc., Torrance, California

[¶] Now at Teralux Engineering, Redondo Beach, California

demonstrated the increased reliability of silicon nitride tensile specimens processed from a slurry passed through a 5 μm filter prior to forming via slip casting. [3]

Here, we show that a commercial silicon nitride slurry, containing the additives needed for densification and grain growth control, can be rapidly converted into a shape using a method called Colloidal Isopressing, recently introduced by Yu and Lange. [4] The primary advantages of shape forming using Colloidal Isopressing are: 1) strength degrading heterogeneities can first be removed by filtering a dispersed slurry, 2) a short forming period, 3) high relative density and complex shapes, 4) no shrinkage during drying, 5) uniform relative density, and thus no shape distortion during densification, and 6) the use of conventional dewatering presses and cold isostatic presses.

Colloidal Isopressing relies on a weakly attractive interparticle pair potential which enables a plastic-to-elastic consolidation phenomenon discovered by Franks and Lange. [5] A weakly attractive (coagulated) particle network can be produced by developing a short-range repulsive potential that is summed with the always present van der Waals attractive potential. [6] There are two general ways of producing a short-range repulsive potential. The first method, used by Yu and Lange to first demonstrate the Colloidal Isopressing method for alumina powders, is based on the electrostatic double layer phenomenon to produce a repulsive potential. In this method, a highly repulsive interparticle potential is produced with a surface charge that causes the particles to be shrouded with counterions. The long range repulsive potential is transformed into a short range repulsive potential by adding excess counterions (i.e. adding salt) to reduce the effective thickness of the counterion cloud, and thus, reduce the interparticle separation distance where the particles become strongly repulsive.

In the second method, small molecules are attached to the surface of the particles to produce a steric repulsion at short separation distances when the particles are attracted to one another via the van der Waals potential.

The method used here is a combined electro-steric effect where the molecules adsorbed onto the surface may ionize and create an effective surface charge. Aqueous processing of silicon nitride requires special consideration due to both the oxidation of silicon nitride in water and the dissolution of the silanol groups on the surface of silicon nitride. [7] Colic et al. [8] showed that the reaction of water with the silicon nitride surface can be decreased substantially by chemisorbing organofunctional silanes at the silanol sites. The aminosilane molecules used for this task also develop a charge, which can also be used to impart a repulsive potential due to an electrostatic double layer in addition to the steric repulsion imparted by the 'brush' configuration of the molecules on the surface.

The 'coated' silicon nitride particles needs to be fully dispersed prior to removing heterogeneities by filtration and then coagulated prior to consolidation. The silicon nitride slurry formulated with the aminosilane can be dispersed by controlling the pH. The addition of salt to a slurry then changes the long range repulsive potential to a short range repulsive potential. In this paper, we apply the Colloidal Isopressing forming technology to a commercial silicon nitride aqueous slurry. The silicon nitride particles are coated with an ionizable organofunctional silane and coagulated with salt. This system provides for the protective coating to keep the silicon nitride from reacting with water, the long range repulsive potential needed to remove the heterogeneities, and then, the weakly attractive interparticle interaction required for Colloidal Isopressing.

Experimental Procedure

All the experiments were carried out with a commercial slurry supplied Allied Signal, Inc (called AS800). The solid content of the slurry was primarily silicon nitride (0.42 volume fraction) plus small fractions of proprietary densification additives. Slurries from three different batches (A, B, and C) were used. An organosilane, N-[(triethoxysilyl)propyl]-O-polyethylene oxide urethane (abbreviated here as PEG-silane) with the chemical formula $C_{10}H_{21}NO_4SiO(CH_2CH_2O)_{4.6}H$ (Gelest Inc., Tullytown, PA), was added to the slurry (2 wt% based on the silicon nitride content). Two different salts were added to different slurries: tetramethylammonium chloride (TMACl, 97%) and tetramethylammonium nitrate (TMANO₃, 96%) (Sigma Aldrich, Milwaukee, WI). The pH was adjusted by adding either nitric acid (HNO₃) or tetramethylammonium hydroxide (TMAOH).

The zeta potential (Zeta Meter System 3.0, Zeta Meter Inc., Long Island City, NY) of an AS800 slurry containing 2 wt % PEG-silane was measured after dilution with deionized water to a powder concentration of 0.025 g/L. The solution was solicited at pH 11 using an ultrasonic horn (Model W-380, Heat Systems-Ultrasonics Inc., Piscataway, NJ). The velocity of the particles under an applied electric field was first measured at the pH 11, then the pH was decreased stepwise by adding HNO₃.

Viscosity measurements were made with a stress-controlled rheometer (Model DSR, Rheometrics Inc., Farmingdale, NY) using slurries diluted to 20 vol% solid using a cup and couette cell (cup diameter 32.0 mm, bob diameter 29.5 mm, bob length 44.0 mm). The dependence of the viscosity on the strain rate was measured for slurries with different salt concentrations (0.0 M, 0.1 M, 0.25 M, 0.50 M, 0.75 M and 1.0 M). All measurements were initiated at the highest strain rate.

The slurries were consolidated by pressure filtration. Two different cylindrical dies were used, having an internal diameter of 25.4 mm and 45.0 mm. Using a hydraulic press (Carver Laboratory Press, Fred S. Carver Inc., Menomonee Falls, WI), a constant pressure was applied to the particle network in the slurry until the consolidation was terminated. The applied pressures ranged from 0.5 MPa to 50 MPa. The equilibrium relative density was reached when the plunger stopped moving with no detectable movement of the plunger for at least one hour.

After pressure filtration, some consolidated slurries were fluidized and then characterized via dynamic rheology using the DSR rheometer. The high relative density and high viscosity consolidated slurry required the use of a 4-blade vane tool (cup diameter 32.0 mm, bob diameter 16.0 mm, bob length 31.0 mm) to avoid slip.[9] To prevent the fluidized body from drying during the rheology measurements, it was covered with a layer of mineral oil. Dynamic frequency sweep experiments were performed to measure the shear modulus, and dynamic stress sweep tests to determine the yield stress. The yield stress was defined as the point at which the storage modulus, G' , starts to decrease substantially as the shear stress increased. The shear modulus was determined by measuring G' at a stress much lower than the yield stress, at which the network exhibits elastic behavior. The measurements were taken after designated periods in order to study the time-dependence of the shear modulus.

Uniaxial compression tests were carried out on consolidated powder compacts saturated with water (diameter 25.4 mm, lengths varying from 25.3 to 27.4 mm, depending on the applied pressure). The specimens were stored in a plastic bag containing a wet paper towel in order to prevent them from drying. A mechanical testing machine (Instron 1123, Instron Co., Canton,

MA) with a 5000 lb. load cell was used for these measurements. All specimens were tested with a displacement rate of 1 mm/min and within one hour after the consolidation. Nominal stresses and engineering strains were calculated from the recorded load-displacement data. The engineering strain was calculated by dividing the displacement by the initial specimen height; the nominal stress was determined by dividing the load by the instantaneous cross-sectional area of the specimen. The instantaneous cross-sectional area was estimated by assuming that the volume of the specimen was unchanged during the experiment. The maximum observed nominal stress was considered to be the peak stress.

Consolidated bodies were liquefied either by hand pressure or with a vibrator table (CM-30, Cleveland Vibrator Company, Cleveland, OH). The liquefied bodies were then injected into silicone molds, containing a rectangular cavity. The filled molds were placed into an isostatic press (Model # IP-2-22-60, Autoclave Engineers Inc., Erie, PA) under 200 MPa for 1 minute. Partially sintered alumina pieces, placed within the silicone mold, were used as porous bodies to remove excess water from the fluidized bodies during isopressing.

The relative densities of the specimens in the filter-pressed and the isopressed state were determined with the weight difference method. To determine the residual amount of water after isopressing, the specimens were weighed before and after drying at 70°C. They were then heating to 500_C to estimate the amount of residual organic additives.

Results

The zeta potential for the AS800 (see Figure 1), reacted with 2 wt% PEG-silane, measured after two weeks and seven weeks after its commercial preparation, were different at pH values greater than the iso-electric point (iep) by nearly a factor of 2 (larger after 7 weeks), whereas their iep was nearly identical ($\text{pH} = 5.5 \pm 0.3$). The zeta potential for batch A and batch B measured two weeks after their preparation were also different at $\text{pH} > \text{iep}$; both had a similar iep.

Figure 2 reports the viscosity versus strain rate data (batch A) for slurries prepared at the iep, in the dispersed state (at pH 10.1), and at pH 10.1 with the addition of different concentrations of either TMACl (Fig. 2a) or TMANO₃ (Fig. 2b). The slurry in the dispersed state ($\text{pH} = 10.1$) without added salt exhibited a very low viscosity and a nearly Newtonian behavior. In the flocced state, the AS800 slurry had a very high viscosity and exhibited strong shear rate thinning behavior. The addition of salt to a dispersed system caused an increase in the viscosity and a change from a nearly Newtonian behavior to a shear rate thinning behavior which is typical for attractive particle networks. No further changes in viscosity were observed for salt addition in excess of 0.5 M.

All bodies consolidated from coagulated slurries at 2 MPa (conditions shown in Table I) could be easily fluidized by vibration. Table 1 shows the values for the initial shear moduli and the average yield stresses of AS800 for these fluidized bodies. All data in Table 1 was obtained by dynamic stress sweep experiments at a frequency of 1.0 rad/s. The shear moduli shown in Table 1 were measured immediately after the vane tool had been plunged into the slurry. The shear moduli were also determined after increasing rest periods within the instrument by performing frequency sweep tests at a stress of 50 MPa. The time-dependence of the shear modulus for a specimen from batch C which contained 2 wt% PEG-silane and 0.5 M TMANO₃

(consolidated at 2 MPa, then fluidized by vibration) is shown in Figure 3. After sequentially determining the elastic modulus of the network for 21 hours, the slurry was stirred again by oscillating the vane at a large amplitude. The shear modulus dropped again to the initial value and showed a similar increase with time (shown as 2nd run in Fig. 3).

Although the specimens consolidated at 2 MPa could be liquefied by vibration, as shown in Fig. 4 they did not exhibit a low flow stress when the consolidated bodies were loaded in uniaxial compression at a displacement rate of 1 mm/min. Nevertheless, their behavior was different than truly brittle specimens. The bodies consolidated at a pressure higher than 5 MPa showed a steeper slope in the elastic regime, a higher peak stresses, and much more cracking than those consolidated at a pressure \leq 5 MPa, as shown by the insert in Fig. 4. Pieces of the specimens consolidated at \leq 5 MPa could be liquefied after mechanical testing, whereas the fractured portions of the bodies consolidated at higher pressures only broke into smaller and smaller pieces during vibration.

The relative densities of the specimens used for the uniaxial compression tests are plotted as a function of the consolidation pressure in Figure 5. A sudden increase in the relative density between 5 and 10 MPa can be recognized. Between these two pressures the behavior of the consolidated slurry changes from plastic to brittle as well.

The relative densities after pressure filtration at 2 MPa and after isopressing at 200 MPa are shown in Table 2. The relative density of the as-received AS800 was measured to be 0.405. The specimen with 2 wt% PEG-silane, without added salt had a high packing density after the consolidation but exhibited a brittle behavior, and thus, could not be liquefied and extruded into the rubber cavity for isopressing. The bodies with 2 wt% PEG-silane and 0.5 M salt could be liquefied for isopressing, and showed a moderate relative density. As shown, isopressing at 200 MPa for 1 minute caused an increase in relative density from \approx 0.51 to \approx 0.60.

Discussion

As expected, the powder in the dispersed slurry formulated at a pH far from the iep without added salt produces the highest relative density and exhibits brittle behavior, consistent with observations of Franks and Lange. [5] Adding a modest amount of salt to the dispersed slurry resulted in a lower relative density after consolidation, but, when consolidated at pressures $<$ 5 MPa, produced bodies that could be fluidized. The fluidized bodies could be injected into rectangular rubber molds and isopressed to a much higher relative density similar to that previously reported for alumina.[4]

Slurries formulated at the iep had higher viscosities relative to those formulated at pH 10 with added salt. At the iep, the particles are strongly attracted to each other by van der Waals forces. Hence the force to pull the particles apart (to move them past each other in a shear flow field) is larger for slurries formulated at the iep, relative to the weakly attractive networks formed by adding salt to a dispersed slurry. According to Figures 2(a) and (b) an addition of 0.5 M of either TMACl or TMANO₃ is sufficient to change the interparticle pair potential from fully repulsive to weakly attractive.

The elastic modulus of the fluidized, consolidated bodies was observed to increase with time (Fig. 3). When the body was stirred at a high shear strain, the low value of the modulus was recovered, and it retraced the same increase found for the first set of measurements. Our results

show that the elastic modulus of the fluidized, consolidated bodies still increased after 20 hours (Fig. 3). That is, the elastic modulus of the consolidated and fluidized body strongly depends on the shear history. The reason for this behavior has been recently discussed by Yu and Lange,ⁱ who suggest that during shear flow, the particles align themselves with the flow field to produce an anisotropic parietal network that relaxes to its isotropic structure when the shear strain is removed. It was shown that the time required to recover the isotropic network was dependent on the strength of the attractive pair potential. [11]

Conclusions

AS800 is a commercial slurry formulated by Allied Signal. Its primary ingredient is silicon nitride; it also contains small fractions of other powders needed for densification and microstructure control. It has been demonstrated that the AS800 slurry could be reformulated to produce shapes via the new Colloidal Isopressing method. Measurements of the shear modulus and the relative density of consolidated AS800 slurries indicate that increasing the PEG-silane content to 2 wt% was sufficient to produce steric repulsion between the silicon nitride particles. Viscosity measurements showed that a salt concentration of either 0.5 M TMACl or TMANO₃ is sufficient to change the interparticle pair potential from fully repulsive to weakly attractive. Consolidation at a pressure of 2 MPa produced a relative density of ≈ 0.51 . A plastic-to-brittle transition of the saturated AS800 powder compacts appears to occur between consolidation pressures of 5 and 10 MPa. Dynamic rheology experiments on AS800 slurries which were consolidated at a pressure ≤ 5 MPa and liquefied beforehand indicated in a time dependent network strength as observed via elastic modulus measurements. The relative density could be increased to ≈ 0.60 after shape forming via Colloidal Isopressing. Finally, isopressed bars were sintered to full density at Allied Signal via pressureless sintering.

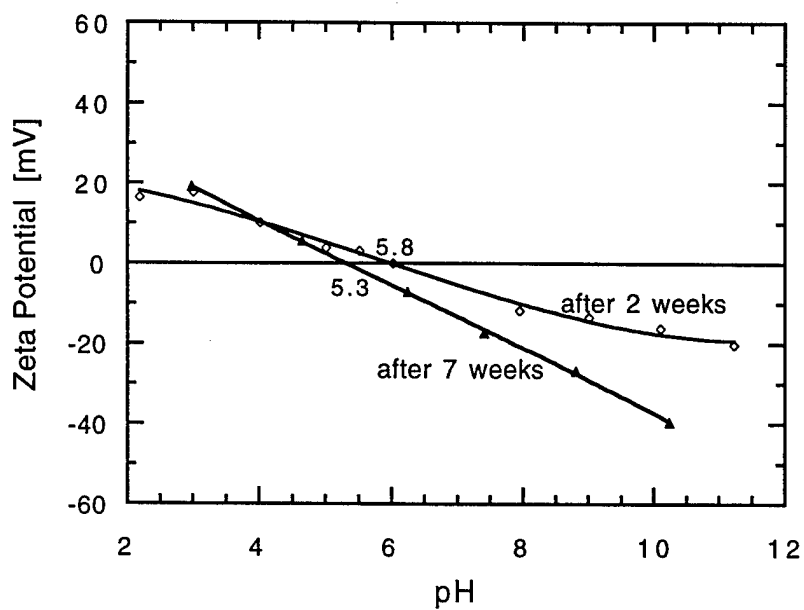
Acknowledgements

We gratefully acknowledge the support for this research from the SRI/DARPA Solid Freeform Fabrication and Design Program, Award number 46-000123, Army Research Office, Contract Number, DAAG55-98-1-0455, and Ceramic Components Division, AlliedSignal Aerospace, Torrance, CA.

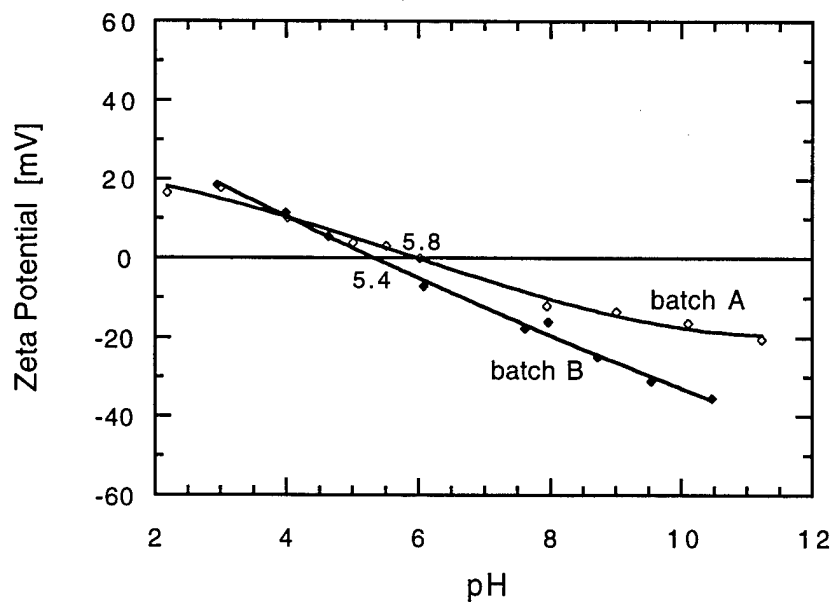
References

- 1 M. Savitz, "Commercialization of Advanced Structural Ceramics," *Am. Ceram. Soc. Bull.*, **78** [1] 53-56 (1999).
- 2 F. F. Lange, "Powder Processing Science and Technology for Increased Reliability," *J. Am. Ceram. Soc.*, **72** [1] 3-15 (1989).
- 3 V. K. Pujari, D. M. Tracey, M. R. Foley, N. I. Paille, P. J. Pelletier, L. C. Sales, C. A. Willkens and R. L. Yeckley, "Reliable Ceramics for Advanced Heat Engines," *Am. Ceram. Soc. Bull.*, **74** [4] 86-90 (1995).
- 4 B.C. Yu and F.F. Lange, "Colloidal Isopressing: A New Shape Forming Method," in press, *Adv. Mater.* (2000).
- 5 G.V. Franks and F.F. Lange, "Plastic-to-Brittle Transition of Saturated Alumina Powder Compacts," *J. Am. Ceram. Soc.*, **79** [12] 3161-68 (1996).

- 6 F. F. Lange, "Colloidal processing of powder for reliable ceramics, " *Solid State + Mat. Science*, 3 [5] 496-500 (1998)
- 7 L. Bergstrom and E. Bostedt, "Surface Chemistry of Silicon Nitride Powders: Electrokinetic Behavior and ESCA Studies," *Colloids Surf.*, 49 183-97 (1990).
- 8 M. Colic, G. V. Franks, M. L. Fisher and F. F. Lange, "Compositionally Dependent Si 2p Binding Energy Shifts in Silicon Oxynitride Thin Films," *J. Am. Ceram. Soc.*, 69 [4] 314-16 (1986).
- 9 J. A. Yanez, T. Shikata, F. F. Lange and D. S. Pearson, "Shear Modulus and Yield Stress Measurements of Attractive Alumina Particle Networks in Aqueous Slurries," *J. Am. Ceram. Soc.*, 79 [11] 2917-24 (1996).
- 10 Q. D. Nguyen and D. V. Boger, "Yield Stress Measurement for Concentrated Suspensions," *J. Rheol. (N.Y.)*, 27 321-49 (1983).
- 11 B.C. Yu and F.F. Lange, "Characterization of Consolidated Alumina Slurries for Colloidal Isopressing," to be submitted to *J. Am. Ceram. Soc.*



(a)



(b)

Fig. 1. (a) Zeta potential of AS800 powder reacted with 2 wt% PEG-silane aged for two periods (batch A) and (b) for two different batches (aged less than two weeks).

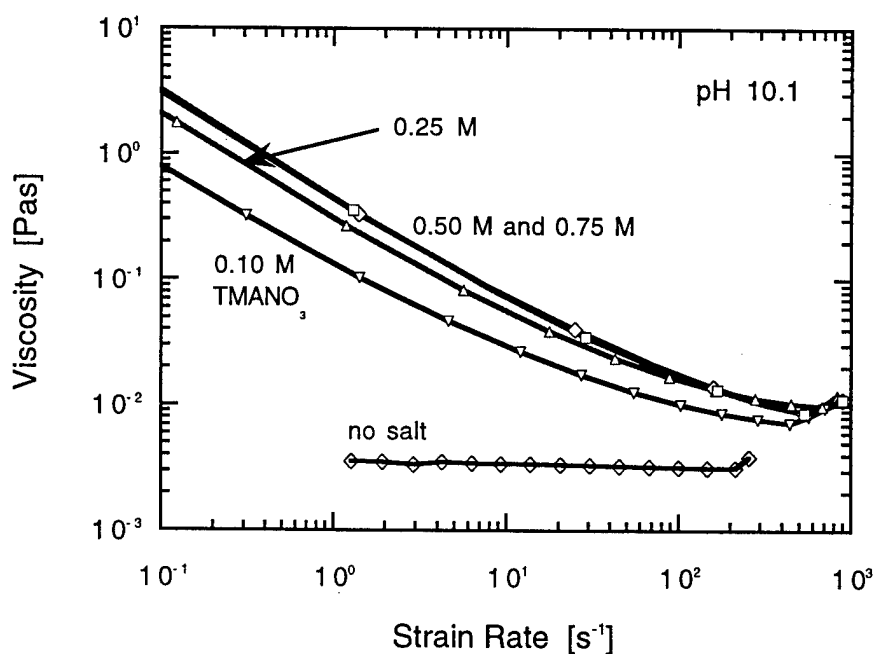
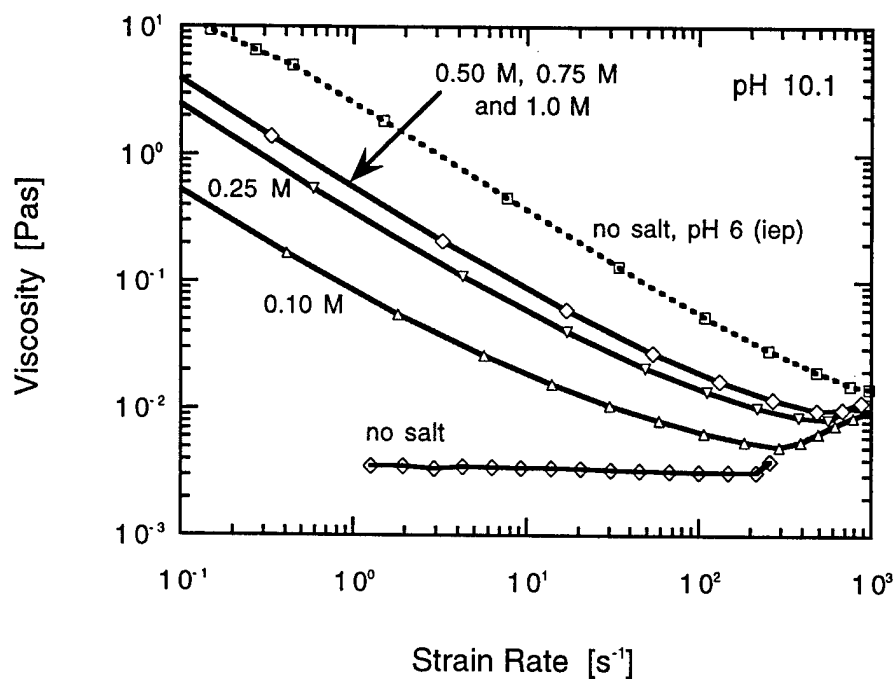


Fig. 2. Viscosity of AS800 (batch A, 2 wt% PEG-silane) diluted to 20 vol%: (a) in the flocced state (at pH 6), in the dispersed state (at pH 10.1), and for slurries formulated at pH 10.1 containing different concentrations of TMACl; and (b) in the dispersed state (at pH 10.1), and for slurries formulated at pH 10.1 containing different concentrations of $TMANO_3$.

batch	A	A	A	B
PEG-silane [wt%]	2	2	1	2
salt	TMACl	TMANO ₃	TMANO ₃	TMANO ₃
salt concentration [M]	0.5	0.5	0.5	0.5
pH	10.1	10.1	10.1	8.7
consolidation pressure [MPa]	2	2	2	2
initial shear modulus [MPa]	1.3	0.9	13	4.5
average yield stress [Pa]	294	406	213	684

Table 1. Shear moduli and yield stresses of consolidated slurries for different compositions.

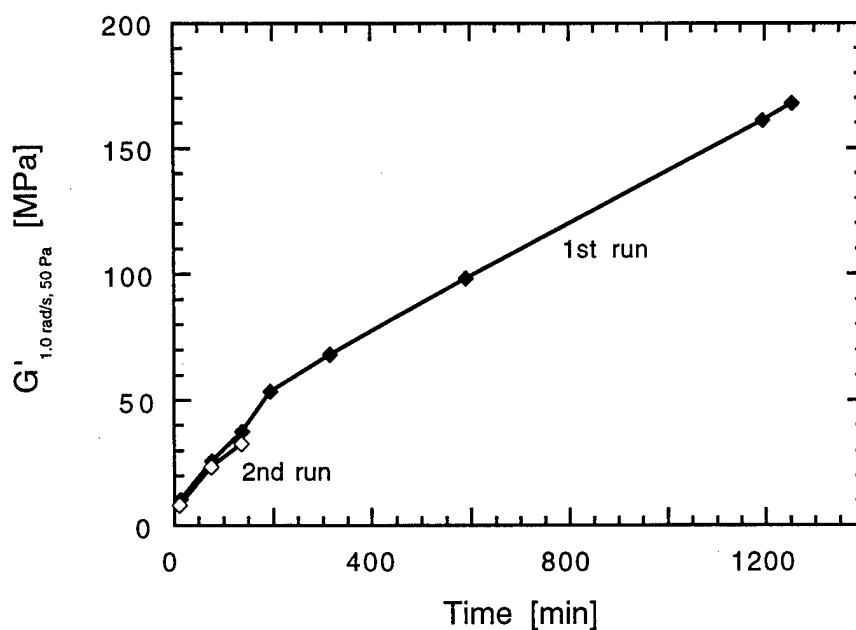


Fig. 3. Increase of the elastic modulus with time for a consolidated body of AS800 (batch C) with 2 wt% PEG-silane and 0.5 M TMANO₃ (consolidation pressure: 2 MPa).

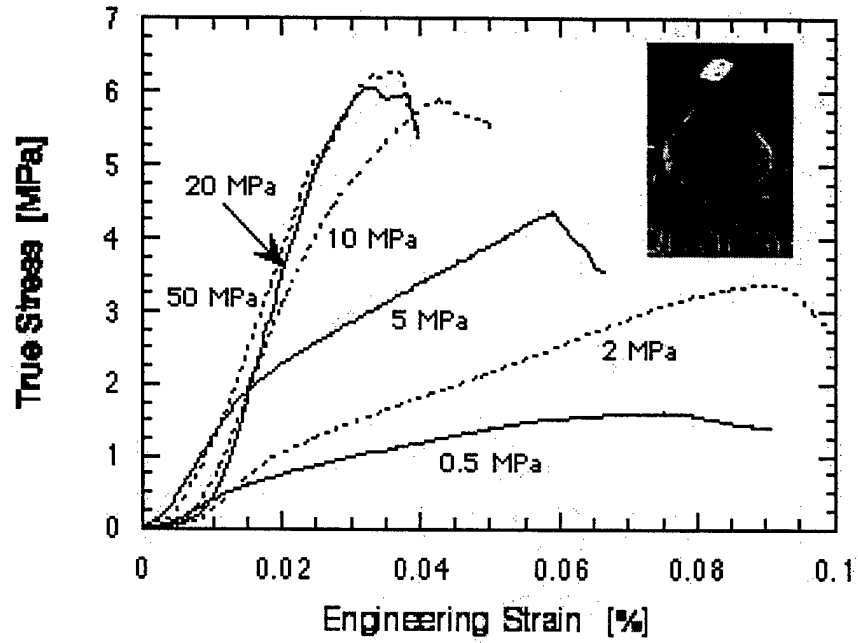


Fig. 4. True stress versus engineering strain curves for different consolidation pressures (AS800, batch B, 2 wt% PEG-silane, 0.5 M TMANO₃, loading rate: 1 mm/min).

batch	PEG-silane [wt%]	salt	salt conc. [M]	pH	rel. density filter-pressed [%]	extrudable?	rel. density isopressed [%]
A	2	-	-	10.1	57.9	no	
A	2	TMANO ₃	0.5	10.1	51.8	yes	60.1
B	2	TMANO ₃	0.5	8.7	51.3	yes	61.7

Table 2. Relative densities after pressure filtration at 2 MPa and after isopressing at 200 MPa for one minute.

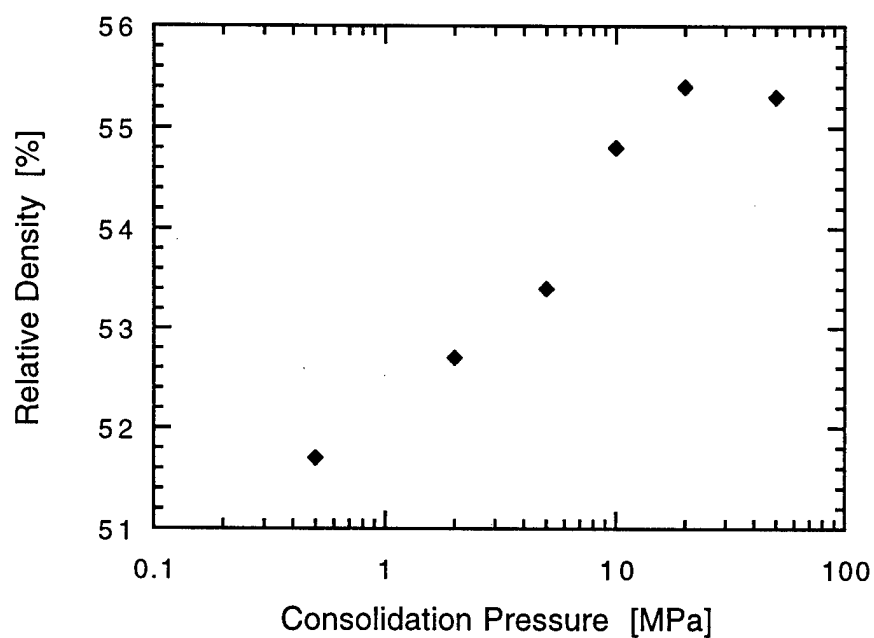


Figure 5. Relative density versus consolidation pressure (AS800, batch B, 2 wt% PEG-silane, 0.5 M TMANO₃).